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Vol. VIII

TRANSCRIPT OF RECORD

PATENT EXHIBITS

Supreme Court of the United States

OCTOBER TERM, 1930

No. 378

STANDARD OIL COMPANY (INDIANA), STANDARD OIL COMPANY (NEW JERSEY), STANDARD DEVELOPMENT COMPANY, ET AL., APPELLANTS,

vs.

THE UNITED STATES OF AMERICA

APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE NORTHERN DISTRICT OF ILLINOIS

FILED AUGUST 23, 1930

(35,300)

(35,300)

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APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE NORTHERN DISTRICT OF ILLINOIS

VOL. VIII

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JUDD & DETWEILER (INC.), PRINTERS, WASHINGTON, D. C., OCTOBER 6, 1930

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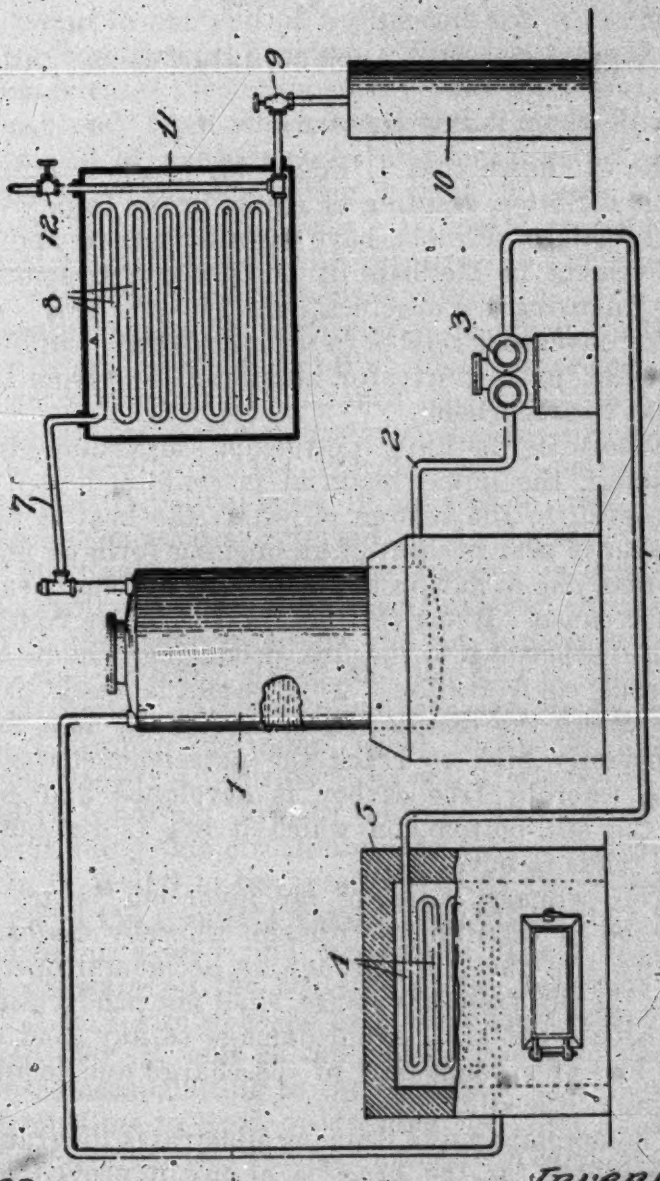
[fol. 1174] PETITIONER'S EXHIBIT 177

E. M. CLARK.

METHOD OF DISTILLING PETROLEUM.

APPLICATION FILED APR. 20, 1914.

1,119,496. Patented Dec. 1, 1914.



Witnesses.
E. C. Clark.
Lin. C. Brown

Inventor:
Edgar M. Clark.
By Dyrenforth, Lee, Christie & Miller.
Attys.

[fol. 1175]

United States Patent Office

Edgar M. Clark, of Alton, Illinois

Method of Distilling Petroleum.

1,119,496. Specification of Letters Patent. Patented Dec. 1, 1914

Application filed April 20, 1914. Serial No. 833,243

To all whom it may concern:

Be it known that I, Edgar M. Clark, a citizen of the United States, residing at Alton, in the county of Madison and State of Illinois, have invented a new and useful Improvement in Methods of Distilling Petroleum, of which the following is a specification.

My invention relates to an improvement in distilling petroleum, particularly for obtaining therefrom low-boiling-point hydrocarbons.

Where in distilling petroleum, according to common practice, the liquid material is contained in a reservoir-like still, to the bottom of which the heat is applied, the danger is ever present of an opening forming in the boiler-bottom, due to flaw in the metal, the bottom burning out, or other cause. When this occurs, the entire contents of the still discharge into the fire, producing a more or less disastrous conflagration. This result is more likely to ensue where the distillation is carried on at a temperature sufficiently high to crack the petroleum-contents of the still, whereby free carbon is developed and accumulates on the still-bottom, on which it lies in red-hot condition and tends to burn it out.

The primary object of my invention is to provide a method of distilling petroleum, whereby discharge of the contents of the still, through an accidental opening occurring therein from any cause, shall not produce serious consequences but shall avoid damage of any kind other than the loss of a small part of the charge and temporary disabling of the still.

The accompanying drawing illustrates diagrammatically, as suitable for the practice of my improved method, an equipment of apparatus involving a so-called pressure-still, in which the distillation is carried on under high tem-

perature (of 650° to 850° F.) and a pressure of 3 to 7 atmospheres produced by the vapors discharging from the still.

At 1 is shown an upright tank or reservoir supported in elevated position and having a rounded bottom, from above which leads a pipe 2 containing a force-pump 3, of any suitable construction. This pipe leads from the discharge-side of the pump to one end of a pipe-coil 4 in a furnace 5, which is preferably coal-burning. The opposite end of the coil communicates through a pipe 6 with the reservoir 1 at its upper end, from which leads a discharge-pipe 7 to the upper end of a water-cooled condenser-coil 8, the discharge-end of which, containing a valve 9, leads to a receiving-drum 10 for the distillate. A pipe 11 rises from the lowermost branch of the coil 8 through the condenser-tank, above which the pipe contains a valve 12.

The apparatus shown is particularly designed for the manufacture of gasolene by distilling under pressure the residue of petroleum-distillation, such as fuel-oil, to produce it. It is to be understood, however, that my invention is applicable generally to the distillation of petroleum while it has peculiar advantages in connection with the pressure-distillation process referred to. In the apparatus illustrated, the liquid material to be distilled is charged into the reservoir, which may contain several thousand gallons. With the pump in action and the furnace going, the valves 9 and 12 being closed, the contents of the reservoir are circulated, passing from the reservoir by way of the pipe 2 through the pump, which forces the liquid in a relatively-fine stream through the coil 4, whence it returns in heated condition through the pipe 6 to the reservoir. By continuing this circulation, the heated liquid returning from the coil 4 to the reservoir heats the contents of the latter and the resultant vapors pass off through the upwardly-inclining pipe 7 and condenser. These vapors build up a pressure on the contents of the reservoir of from about 3 to 7 atmospheres and raise their temperature to about 650° F. and as the run proceeds, to about 850° F. Gases accumulating in the condenser are allowed to escape from time to time, on opening the valve 12, for relieving the gas-pressure, which is liable to accumulate in the coil and obstruct the action of the apparatus. From time to time the valve 9 is opened for discharging the dis-

tillate into the drum 10. This distillate is crude gasolene of superior quality and it may be subjected to further treatment, well-known in the art, for refining it.

By thus subjecting to the action of heat the material under treatment in a relatively fine stream, while free carbon is formed in the liquid passing through the coil 4, it courses under the high pressure at which the liquid is circulated [fol. 1176] so rapidly through the same as to prevent accumulation therein of the carbon, which it carries back into the reservoir in the bottom of which it may accumulate without injurious effect, since there is no fire under the reservoir. Should, however, a leak accidentally occur in the coil, so little of the liquid will discharge into the fire in the furnace that no damage will ensue. My improved method, therefore, not only greatly decreases the danger of accident, but if the latter occurs the resultant damage is comparatively immaterial. Moreover, it enables from 3 to 7 runs to be made of the still without requiring the apparatus to be stripped and cleaned, whereas where the boiler 1 is fired but one run can be made without stopping and cleaning the carbon deposit out of it.

While a pump is shown for circulating the liquid material, any other way of producing the necessary rapid circulation is intended to be within my invention.

What I claim as new and desire to secure by Letters Patent is:

1. The method of distilling petroleum, which consists in circulating it forcibly and rapidly in a relatively-small stream under confinement and subjection to a cracking temperature from and back to a bulk-supply of the liquid material, taking off and condensing the resultant vapors and maintaining a pressure of said vapors on said supply.

2. The Method of distilling liquid residue of petroleum-distillation, which consists in circulating said liquid forcibly and rapidly in a relatively-small steam and under confinement and subjection to heat from and back to a bulk-supply of the residue, taking off and condensing the resultant vapors and maintaining said liquid at a temperature of from about 650° F. to about 850° F. under a pressure thereon of said vapors of about 3 to 7 atmospheres.

3. The method of distilling liquid residue of petroleum-distillation, which consists in circulating said liquid forcibly

and rapidly in a relatively-small stream under confinement and subjection to heat from and back to a bulk-supply of the residue, taking off and condensing the resultant vapors and maintaining said liquid at a temperature of from about 650° F. to about 850° F. under a pressure thereon of said vapors of about 3 to 7 atmospheres exerted throughout their course to and during condensation.

Ergar M. Clark.

In presence of Nellie B. Dearborn, Daisy C. Thorsen.

Correction in Letters Patent No. 1,119,496

It is hereby certified that Letters Patent No. 1,119,496, granted December 1, 1914, upon the application of Edgar M. Clark, of Alton, Illinois, for an improvement in "Methods of Distilling Petroleum," was erroneously issued to the inventor, said Clark, whereas said Letters Patent should have issued to Standard Oil Company, of Whiting, Indiana, a corporation of Indiana, as assignee of the entire interest in said invention, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of December, A. D., 1914.

J. T. Newton, Acting Commissioner of Patents. (Seal.)

[fol. 1177] PETITIONER'S EXHIBIT 178

R. E. HUMPHREYS.
METHOD OF DISTILLING HYDROCARBONS.
APPLICATION FILED JUNE 29, 1914.

1,119,700. Patented Dec. 1, 1914.

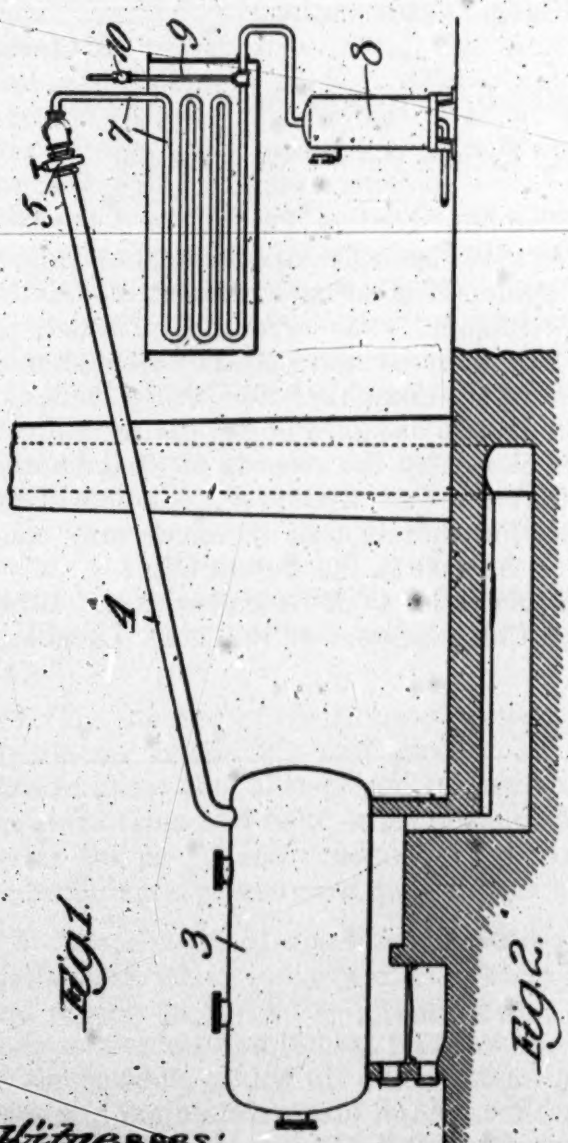


Fig. 1.

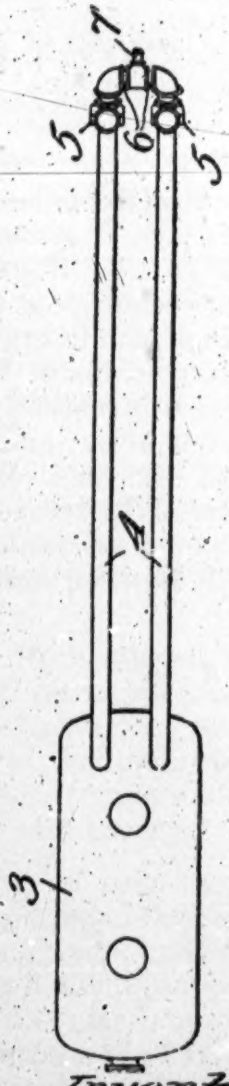


Fig. 2.

Witnesses:

Inventor:
Robert E. Humphreys
By Dyrenforth, Chritton & Hale
Attys.

[fol. 1178] United States Patent Office

Robert E. Humphreys, of Whiting, Indiana, Assignor to Standard Oil Company, of Chicago, Illinois, a Corporation of Indiana

Method of Distilling Hydrocarbons

1,119,700. Specification of Letters Patent. Patented Dec. 1, 1914

Application filed June 26, 1914. Serial No. 847,412

To all whom it may concern:

Be it known that I, Robert E. Humphreys, a citizen of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful improvement in the Method of Distilling Hydrocarbons, of which the following is a specification.

My invention consists in a novel method for the distillation of hydrocarbons, its object being primarily so to treat hydrocarbons of relatively high boiling-point (such, for example, as the product known in the trade as fuel-oil, a para-fin oil, the boiling point of which is upward of 500° F.), as to produce therefrom hydrocarbons of much lower boiling-point, such as the commercial product known as gasolene which is a para-fin oil of much lower boiling point.

In the practice of my process, in its preferred form, I employ as measures of commercial expediency, all the devices and processes which have been found useful for that purpose. Among these processes and devices may be mentioned the process of the Burton Patent No. 1,049,667, dated January 7, 1913, and the process of my application, Serial No. 813,220, filed January 20, 1914. However desirable these features are in practice, they form no part of my present invention and are, therefore, not here illustrated, but are enumerated in order that those skilled in the art will understand that the highest possibly efficiency requires that the present invention be supplemented by what is now the most approved practice in the same general field.

My process is preferably carried out in an apparatus, such as that herein illustrated, in which—

Figure 1 is a side sectional elevation, and Fig. 2 is a top plan of the apparatus, suitable for carrying out the process.

Referring to the drawings, 3 is a still which may be of ordinary form. Extending obliquely upward from the still is a conduit consisting of two pipes, 4, side by side, each controlled by a valve 5. The pipes 4 communicate with a header 6 which opens into a condenser 7. The condensed products enter a receiving drum 8, and the uncondensed gases pass out through a relief pipe 9 controlled by the valve 10.

The valve in the relief-pipe is so manipulated as to maintain in the system a pressure of upward of 4 atmospheres, so that the distillation takes place at the temperature required by the high pressure thus produced. When the raw material is the commercial product known as fuel oil, the temperature will be upward of 650° F. and the distillate entering the receiving drum 8 will be crude gasolene.

The essence of the present invention is the use of the inclined conduit, consisting of the pipes 4, and in practical operation the use of this inclined conduit, or run-back, as it is commonly termed in practice, is most important. Its operation is as follows: The complicated chemical processes going on in the still produce products of varying gravities, and consequently of varying molecular weights and boiling-points. The fractions vary from non-condensable gases through the light napthas down to fractions which are but slightly lighter than the raw material. The operation of the inclined conduit, or run-back, is to condense the heavier fractions of the distillate and automatically to return them to the still 3 for further treatment therein. In other words, this inclined conduit has the practical effect of subjecting the heavier fractions repeatedly to the action of the pressure and temperature in the still, until the desired molecular re-arrangement has occurred, while permitting those fractions which have already been sufficiently acted upon to pass over and be condensed. It is manifest, therefore, that the size and dimensions of the inclined conduit, or run-back, is of considerable importance, and I may suggest, by way of example that I have found that in the use of a still 8 ft. in diameter and 20 ft. in length an inclined conduit, or run-back, consisting of two pipes each 12 inches in diameter and 40 ft. long produces a distillate of the proper gravity for

crude gasolene. The use of two pipes is advantageous because, when the end of the run approaches and the flow of the vapors is slow, one half the conduit can be closed, so that condensation can be maintained of the proper amount.

While as heretofore stated, I prefer to hold the vapors under pressure throughout their course and while undergoing both the initial and final condensation, as by controlling the relief pipe 9, it is manifest that the pressure control of the final condensation, *i. e.*, the condensation of the light [fol. 1179] vapors which pass from the run-back is not essential to the invention. Such fractional condensation as occurs in the run back itself, however, should evidently be under pressure for the carrying out of my process, as otherwise there would be considerable difficulty in returning the condensed fractions to the still for further treatment therein.

I realize that considerable variation is possible in the details of the process herein shown, and I do not intend to limit myself thereto, except as pointed out in the following claims, in which it is my intention to claim all the novelty inherent in the process as broadly as is permitted by the state of the art.

What I claim as new and desire to secure by Letters Patent is:

1. The method of treating liquid residue of the paraffin series of petroleum distillation having a boiling point of upward of 500° F. to produce therefrom hydrocarbon oils of the same series but of lower boiling points, which consists in distilling the high boiling point hydrocarbons under a pressure of upward of four atmospheres, cooling all the vapors passing from the still while under such pressure to condense the heavier fractions thereof, and simultaneously returning the condensed heavier fractions to the still to undergo therein further treatment, and leading off and condensing the light vapors.

2. The method of treating liquid residue of the paraffin series of petroleum distillation having a boiling point of upward of 500° F. to produce therefrom hydrocarbon oils of the same series but of lower boiling points, which consists in distilling the high boiling point hydrocarbons under a pressure of upward of four atmospheres, cooling all the

vapors passing from the still to condense the heavier fractions thereof and simultaneously returning the condensed heavier fractions to the still to undergo therein further treatment and leading off and condensing the light vapors, maintaining such distillation pressure of upward of four atmospheres on said vapors throughout their course to and while undergoing condensation.

In testimony whereof I have hereunto set my hand this 24th day of June, 1914.

Robert E. Humphreys.

In the presence of two subscribing witnesses: A. C. Fischer, F. A. Florell.

[fol. 1180]

PETITIONER'S EXHIBIT 179

E. M. CLARK.

ART OF PETROLEUM DISTILLATION.

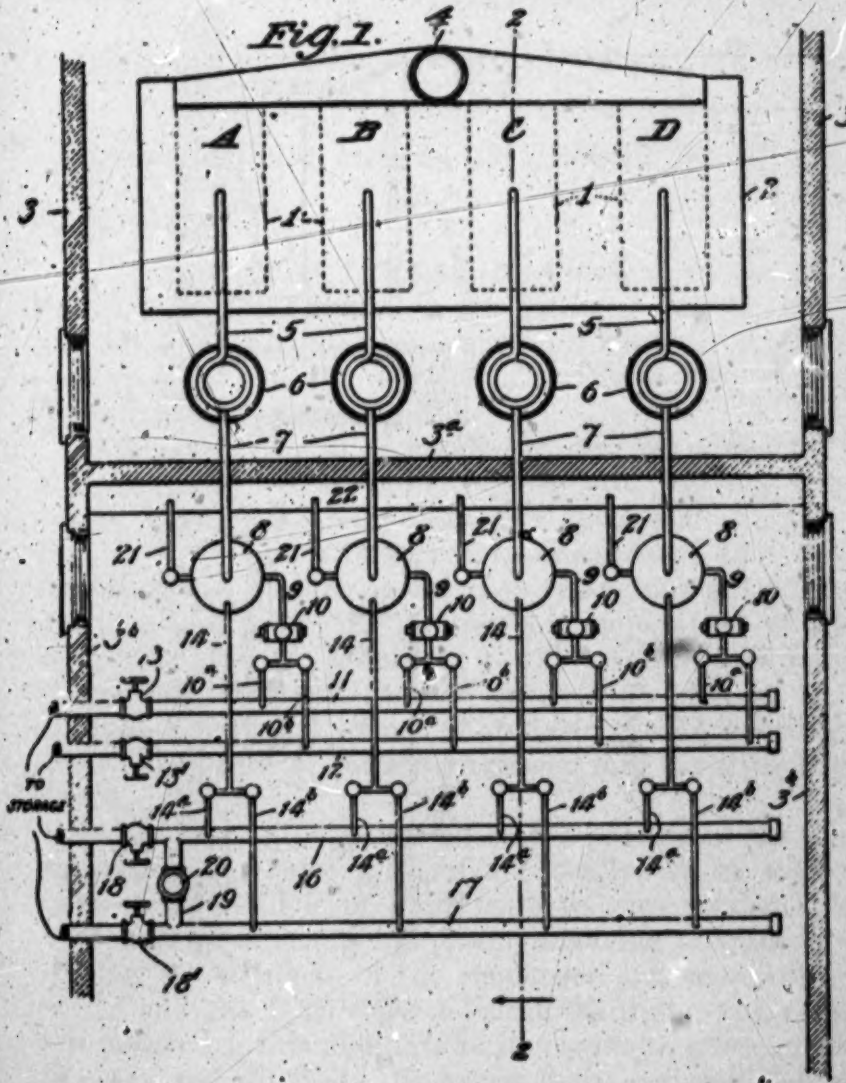
APPLICATION FILED APR. 20, 1914.

1,129,034.

Patented Feb. 16, 1915.

2 SHEETS—SHEET 1.

Fig. 1.



Witnesses.

Inventor:

Edgar M. Clark.

By Fisher, Atkinson & Co. Carlos J. Hills.

Attorneys.

4486

[fol. 1181]

E. M. CLARK.

ART OF PETROLEUM DISTILLATION.

APPLICATION FILED APR. 30, 1914.

1,129,034.

Patented Feb. 16, 1915.

2 SHEETS—SHEET 2

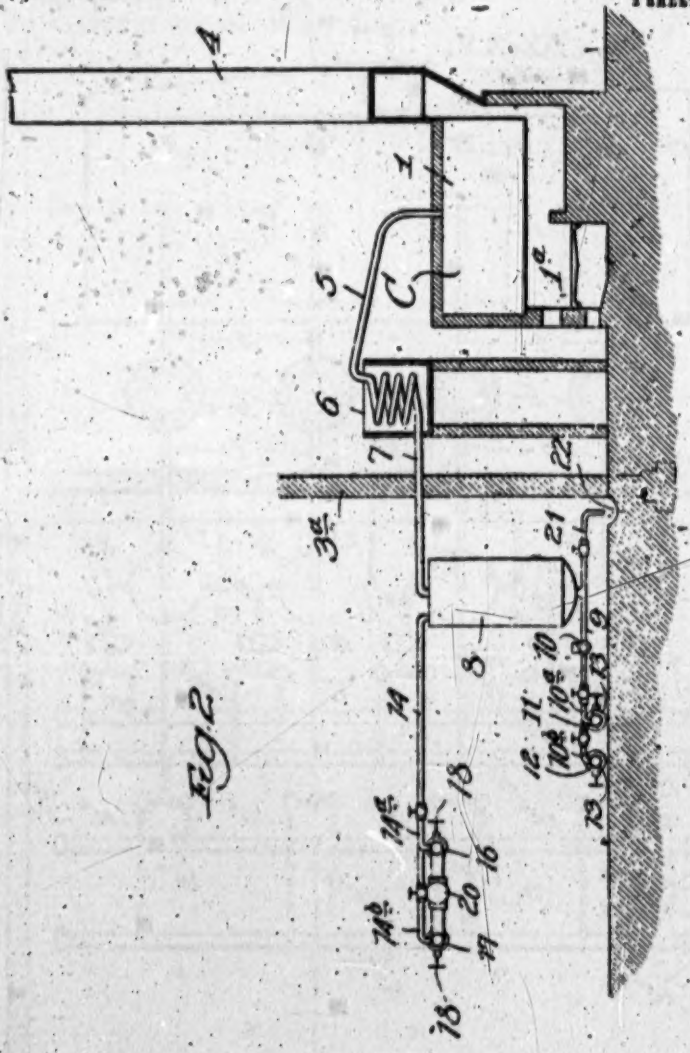


FIG. 2

Witnesses.

Inventor.

Edgar M. Clark.

By Dyrenforth, Lee, Chidester & Miller.

Attys.

PX 179-2

[fol. 1182] United States Patent Office

Edgar M. Clark, of Alton, Illinois, Assignor to Standard Oil Company, of Whiting, Indiana, and Chicago, Illinois, a Corporation of Indiana

Art of Petroleum Distillation

1,129,034. Specification of Letters Patent. Patented Feb. 16, 1915

Application filed April 20, 1914. Serial No. 833,244

To all whom it may concern:

Be it known that I, Edgar M. Clark, a citizen of the United States, residing at Alton, in the county of Madison and State of Illinois, have invented a new and useful Improvement in the Art of Petroleum Distillation, of which the following is a specification.

In the art of distilling residue of petroleum distillation, such as gas oil or fuel oil, at atmospheric pressure, vaporization begins at a temperature of about 250° F., and all will distil over at a temperature upwards of 650° F. In distilling this residue under a pressure upward of three atmospheres, producing a range of temperature of about 650° F. to 850° F., according to the inventions of Letters Patent No. 1,049,667, granted January 7, 1913, to W. M. Burton, a material quantity of fixed gas (amounting to about 2 per cent. of the stock charged into the still) is produced.

In the practical application of the process of the aforesaid patent, a battery of stills (usually ten or more) is used. Each still is provided with its own condenser and with further separate equipment involving a drum for receiving the products of the condenser and separating the water and gas from the condensed distillate, and a meter for measuring this distillate in its course to storage. Both the gas and distillate discharge lines are equipped with valves for controlling the rate of discharge. When a still in the battery is freshly charged and fired, the valves in these discharge lines are closed. As the firing of the still is continued and the temperature of its contents rises to

about 250° F., water and petroleum vapors distil over through the condenser into the receiving drum. As the distillation proceeds small quantities of uncondensed vapor or gas collect in the apparatus, and after a material quantity of low grade distillate (upward of about 8 per cent. of the stock charged) has been produced, sufficient gas has collected in the apparatus to create a pressure of vapors through the condenser. Continued firing of the still raises further the temperature of the contents producing increasing formation of gas and building up of pressure in the apparatus. When the desired temperature (about 650° F.) and pressure (say about 70 to 75 lbs.) have been attained, the gas in the apparatus is allowed to escape slowly through a valve in its discharge line from the top of the receiving drum. Vapors will then begin to come over through the condenser, and high-grade liquefied distillates will be produced and be discharged from the receiving drum through the meter into storage. Since this distillation process is necessarily slow, the formation of gas in very gradual. Production of the high-grade distillate is dependent on constant pressure on the apparatus. A slight drop in pressure causes the vapors to come over more freely and produces low-grade distillate, and, conversely, even a slight increase in pressure entirely stops the flow of vapors with resultant danger to the apparatus.

It is the primary purpose of the present invention to provide for so controlling the discharge of gas and liquefied distillate that a minimum amount of the latter of low grade and a maximum amount thereof of high grade shall be produced.

It is a further purpose to safeguard the apparatus by preventing any extraordinary excess of pressure therein, and also to so apply a gas-pressure of about 70 to 75 lbs. from stills in the battery that are running to the contents of a still when freshly charged as to prevent distillation of such contents before the desired temperature has been attained.

In the accompanying drawings, Figure 1 illustrates diagrammatically, by a plan view, a battery of stills and the equipment that belongs with them for practising the invention in a preferred manner, and Fig. 2 is a view in sectional elevation, the section being taken on line 2, Fig. 1.

Four stills 1, denoted respectively A, B, C and D, are indicated by dotted representation and will suffice for the purposes of the explanation hereinafter given. These stills are shown under a shed 2, between walls 3, and they communicate with a stack 4, common to all, for carrying off products of combustion from the furnaces under the stills, one of these furnaces being represented at 1^a in Fig. 2. A vapor pipe 5 leads from the top of each still to the upper end of the water-cooled coil of a separate condenser 6, and from the bottom of each coil leads, through the inner wall 3^a of a housing, of which the side walls 3^b are shown, a pipe 7 for conducting the products of the condenser, composed [fol. 1183] of liquefied distillates and the light, gaseous products of distillation which have not yielded to the action of the condenser, into a separate drum 8 at the top of the latter. From the bottom of each drum leads a pipe 9 containing a meter 10 for measuring the liquefied distillate and having two valved branches 10^a and 10^b which discharge, respectively, into header-pipes 11 and 12 closed at one end and containing similar shut-off valves 13 and 13′ respectively. These header-pipes discharge to storage-tanks (not shown). Each drum discharges gas from its upper end through a pipe 14 having two valved branches 14^a and 14^b leading, respectively, into header-pipes 16 and 17, which are closed at one end and contain similar shut-off valves 18 and 18′ respectively, these pipes which also lead to storage-tanks (not shown), being connected by a pipe 19 containing a pressure relief valve 20 of any ordinary or suitable type.

At 21 is shown, leading from the bottom of each drum to a gutter 22, a valved pipe for drawing off the watery product of condensation of the vapors generated in the early part of the run.

For the purpose of explanation, let it be assumed that three of the stills 1, namely those denoted as A, B and C, are running at the cracking temperature of upward of 650° F. and under a pressure of about 70 to 75 lbs. of the gases on the contents of the stills. The valves in branches 14^b connected with these three stills are open and the gases are discharging into the header-pipe 17 and are being held back by the partly closed valve 18 in the latter and the relief valve 20, to produce the required pressure of 70 to 75 lbs. in the header-pipe and throughout the apparatus of the

running stills. The valves in the pipes 21 belonging to these three stills are closed, since all watery vapor from them has been distilled off before they reached the cracking temperature. The valves in branches 10^b are open and high-grade liquefied distillate is being discharged from the bottoms of the three respective condensers through the meters into the header-pipe 12 and through its partly open valve 13 to storage. The rate of this discharge is regulated by the valve 13 in the header-pipe 12 to maintain the required pressure throughout the apparatus and discharge the distillate as it is produced. The three stills thus running are all subject to the same pressure by reason of the valves in branches 14^b leading to the header-pipe 17 and the valve in branches 10^b leading to the header-pipe 12 being open. These stills being connected by the header-pipes 17 and 12, give a sufficient volume of gas and liquid distillate to make the rate of their discharge easily controllable by the valves 18′ and 13′. Let it also be assumed that the fourth still, denoted as D, has just been freshly charged and fired. The valve in pipe 21 and the valves in branches 10^a, 10^b and 14^b, belonging to that still, are closed, and the corresponding valve in branch 14^a is opened. The still D is thus closed to the 70 to 75 lbs. pressure maintained in the header-pipes 12 and 17, and is open only to the header-pipe 16, which conducts the gases to storage, or to the furnaces. The firing of this still is continued with resultant rise of temperature of its contents. At about 212° F. the watery portions of these contents are driven over through the respective condenser 6 into the drum communicating therewith. From time to time the valve in the respective pipe 21 is opened to discharge the water into the gutter 22. When the water has all been driven off, which is indicated by the temperature of the contents of the still D, the oil portion thereof will begin to distil over at about 250° F. To stop this distillation and the resultant production of low-grade distillate, the valve in the branch 14^a belonging to the still D is closed and that in the corresponding branch 14^b is gradually opened. This allows the gas from the three other stills, that are running under a pressure of 70 to 75 lbs. in the header-pipe 17, to exert its pressure back through the branch 14^b, belonging to still D, and the interposed equipment upon the contents of that still to stop

the flow of vapors from the latter. In this way the pressure upon the contents of the freshly-charged still is raised to that upon the stills A, B and C. The firing of still D is continued until the temperature of its contents is raised to upward of 650° F., when that still will begin to drive over its gases through the condenser, and drum and branch 14' belonging to it, into the header-pipe 17, and the production of high-grade liquefied distillate will begin. The valve in branch 10^b is now opened and the high-grade distillate produced discharges into the header-pipe 12 in connection with that produced from the other running stills. The four stills are now running in conjunction, all subject to the same control and the same pressure-influences. The sudden generation of excessive or dangerous pressure in one still is prevented by the connection of all through the header-pipes and open valves. Let it further be presumed that a still, say that denoted A, has completed its run and is ready to be drawn off, cleaned and freshly charged. Its furnace-fire is drawn, and the valves in branches 10^b and 14^b are closed thereby shutting it off from the 70 to 75 lbs, pressure in the header-pipes 17 and 12 and from the influence of the stills B, C and D. The valve in the respective branch 14^a is slowly opened to permit the gas to pass through the header- [fol. 1184] pipe 16 to storage or to the furnaces; and the valve in branch 10^a is also opened, to permit low grade or inferior liquefied distillate produced after closing off the header-pipe 17, to pass through the header-pipe 11 to storage. As soon as the gas that was held under 70 to 75 lbs. pressure in the equipment belonging to still A has been discharged, the tar or residual contents of the still are drawn off, and it is made ready to clean and receive a fresh charge. As will be understood each still in a battery is handled in this way after completing its run.

I realize that considerable variation is possible in the details of construction thus specifically shown and described, and I do not intend by illustrating a single, specific, or preferred embodiment of my invention to be limited thereto; my invention being, in the following claims, to claim protection upon all the novelty there may be in my invention as broadly as the state of the art will permit.

What I claim as new and desire to secure by Letters Patent is:

1. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, and a valved header connected with the condensers to receive therefrom the uncondensed gaseous portions of said vapors and confine them under pressure, and means whereby such pressure produced in a late stage of distillation may be used to exert pressure on the material under distillation in an early stage of distillation.

2. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, a header connected with the condensers to receive therefrom the condensed distillate, and a valved header connected with the condensers to receive therefrom the uncondensed gaseous portions of said vapors and confine them under pressure, and means whereby such pressure produced in a late stage of distillation may be used to exert pressure on the material under distillation in an early stage of distillation.

3. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, drums communicating with the lower discharge-ends of the condensers, and a valved header connected with the upper parts of the drums to receive therefrom the uncondensed gaseous portions of said vapors and confine them under pressure, and means whereby such pressure produced in a late stage of distillation may be used to exert pressure on the material under distillation in an early stage of distillation.

4. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, drums communicating with the lower discharge-ends of the condensers and provided with drain-pipes, a header connected with the drums to receive therefrom the condensed distillate, and a valved header connected with the condensers to receive therefrom the uncondensed gaseous portions of said vapors and confine them under pressure, and means whereby such pressure produced in a late stage of distillation may be used to exert pressure on the material under distillation in an early stage of distillation.

5. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, drums communicating with the lower discharge-ends of the condensers, a pair of headers, meter-containing pipes leading from the lower ends of the drums and each having valved branches leading respectively to said headers, a pair of valved headers, and pipes leading from the upper parts of the drums and each having valved branches leading respectively to said valved headers, for the purpose set forth.

6. A petroleum-distilling plant comprising, in combination, a battery of stills, condensers into which the vapors from the stills discharge, drums communicating with the lower discharge-ends of the condensers, a pair of valved headers, pipes leading from the upper parts of the drums and each having valved branches connected respectively with said headers, and a pressure-relief valve in a pipe-connection between said headers.

Edgar M. Clark.

In presence of Ottilie C. Avisus, Nellie B. Dearborn.

[fol. 1185]

PETITIONER'S EXHIBIT 180

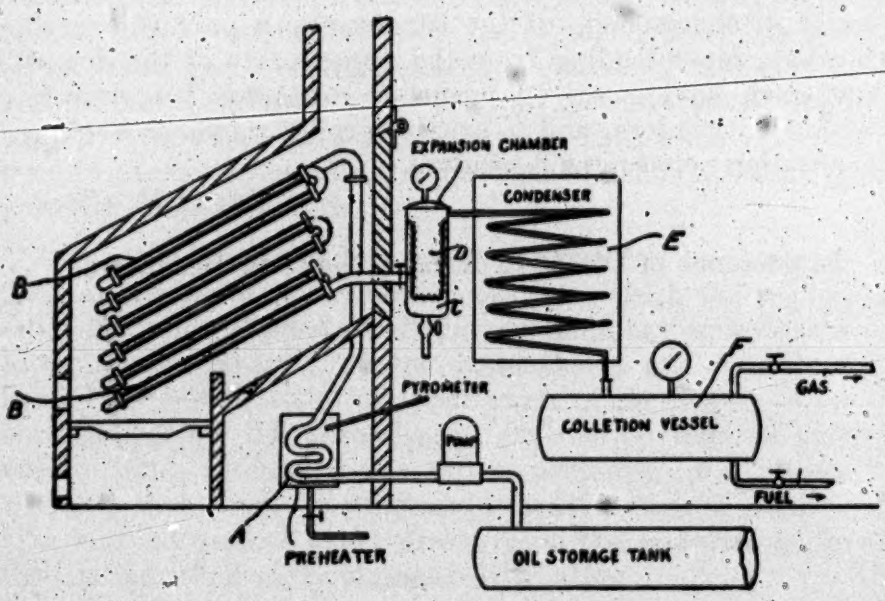
W. A. HALL.

PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBONS INTO LIGHTER HYDROCARBONS.

APPLICATION FILED JULY 24, 1914.

1,175,909.

Patented Mar. 14 1916



Witnesses
H. A. Zelling
Benj. Mudgett

Inventor
William A. Hall
by P. Singer Atty

PX 180-1

[fol. 1186] United States Patent Office

William A. Hall, of New York, N. Y.

Process for the Conversion of Heavy Hydrocarbons into Lighter Hydrocarbons

1,175,909. Specifications of Letters Patent. Patented Mar. 14, 1916

Application filed July 24, 1914. Serial No. 852,965

To all whom it may concern:

Be it known that I, William Augustus Hall, a citizen of the United States Republic, and resident of New York, N. Y., United States of America, have invented a certain new and useful Improvement in Processes for the Conversion of Heavy Hydrocarbons Into Lighter Hydrocarbons, of which the following is a specification.

This invention relates to improvements in the hydrogenation of heavy hydrocarbons with the object of converting them into hydrocarbons of lower specific gravity and boiling point such as can be used successfully in internal combustion engines of the automobile type.

In the practice of other processes of hydrogenation known to me the hydrogenation of the oil has been effected by affixing to the hydrocarbon molecule additional hydrogen derived from some extraneous source, which may be free gaseous hydrogen, or producer gas, or nascent hydrogen from the decomposition of water, the affixation being usually accomplished by the well known catalytic action of nickel or other metal which will act in a similar manner, a process of this general character being claimed in my copending application 769,610, filed May 24, 1913. These processes have been found very expensive as free hydrogen is a costly material, and the N, CO and CO_2 content of producer or water gas has presented difficulties.

The improved process consists in subjecting the volatilized heavy hydrocarbon, in the absence of steam or any extraneous source of hydrogen, either in the form of water, steam or added hydrogen, to the action of heat and pressure in the presence of a catalyst capable of effecting the fixation of hydrogen to hydrocarbons, allowing the prod-

ucts to expand and thereby deposit carbon, and cooling the residual products to produce by condensation a liquid hydrocarbon containing less carbon than the said heavy hydrocarbon, and especially adapted for use in high speed internal combustion engines.

It has also been proposed to pass a mixture of oil and water or steam through tubes containing metallic nickel rods in a retort maintained at a dull red heat. My invention is distinguished from such a process in that I pass the vaporized oil through tubes containing rods of nickel or other hydrogenating catalyst, but with the addition thereto of no hydrogen, and no water or steam.

If the hydrocarbon oil is heated under a moderate pressure, say a pressure of about 5 atmospheres, to a temperature of upward of 600° C., in the presence of the catalyst, and in the absence of steam or any extraneous source of hydrogen, either in the form of water, steam or added hydrogen gas, an efficient conversion of the oil takes place, the oil being partially decomposed and gases set free, such gases being in turn decomposed by the heated catalyst with liberation of hydrogen which in a nascent state is to a considerable extent affixed to the condensable portion of the decomposed hydrocarbon oil.

The catalysts I employ are substances such as the metals, or oxids of the metals, nickel, cobalt, silver, palladium, chromium or manganese, which substances are hereinafter referred to under the term "catalytic body of the nickel type."

Apparatus suitable for the performance of the process is shown diagrammatically in the accompanying drawing.

As shown, the apparatus includes a preheater A for raising the temperature of the oil and to some extent volatilizing the same before it enters the tubular converter B, so that the gas may be produced at as early a stage in the process as possible.

The converter shown is constituted by a serpentine inclined metallic tube so arranged that the circulation is through the top section, then down and through the next, and so on to the bottom, the exposure being at first to the lowest temperature, which is at the top, and gradually increasing toward the bottom. In the tubular elements of the converter is placed the catalytic material which rests

in contact with the heated walls of the tube. From the converter B the products are passed into an expansion chamber C where their temperature is somewhat reduced. The said expansion chamber C may be provided with a metallic gauze screen D, preferably of conical shape, which will collect and extract any loose carbon that may be set free (it being found that such carbon is most readily deposited [fol. 1187] at the point where the expansion occurs and to the greatest extent if the pressure be suddenly reduced from that in the converter (about 5 atmospheres) down to atmospheric pressure). This loose carbon is of course a product of the decomposition and its extraction from the heavy oil to a large extent accounts for the reduction of the specific gravity.

It is to be noted that the pressure of the vapors drops materially, in passing from the converter B to the chamber C. This drop in pressure appears to aid materially in the deposition of free carbon in large quantities in the receptacle C. By causing the carbon to deposit in the receptacle C, instead of in the elements of the converter B, there is no danger of the converter being clogged up by means of this loose carbon.

It will be noted that the gases and vapors produced by the decomposition of the oil, will be caused to flow rather rapidly through the retort, and since the cross section of the space in the retort is rather small, owing to the fact that the metal rod therein takes up quite a large part of the space therein, the current of gases and vapors flowing through the retort will carry along all the free carbon, or soot-like material, consequently not much of this will deposit within the retort. After the pressure falls, and the gases enter the larger chamber C, most all the free carbon will deposit in the expansion chamber C, and on the gauze member D. Tarry matters will likewise be separated in the chamber C. From the said expansion chamber C the products are passed through a cooling condenser E and into a receiving tank F from which can be extracted any fixed gases that have not combined with the condensable portions. The condensate is found to be an entirely different product from the oil started with—it has a much lower specific gravity and boiling point and when redis-

tilled and fractionated yields a large portion of volatile spirit eminently adapted for use in automobiles. For instance if the raw material used be "gas oil" (that being a refinery distillate having a boiling point above the boiling points of petrol and lamp oil) it will yield from 50 to 70% of a fuel of a specific gravity of about .765 with a boiling point which is lower than that of commercial petrol. The product of this process also contains a proportion of unsaturated hydrocarbons. The quantity of unsaturated hydrocarbons may vary more or less, but the quantity is always rather small, as compared with the products of some of the other processes with which I am familiar. Of course it is not necessary to redistil the condensate, as the fractionation can be effected by a dephlegmator situated between the converter and the condenser.

Having described my invention, I declare that what I claim and desire to secure by Letters Patent of the United States is:

1. The herein described method of converting relatively heavy liquid hydrocarbons into lighter and more volatile hydrocarbons, which comprise- the step of vaporizing said relatively heavy hydrocarbons, and causing a current of the vapors to flow, in the absence of extraneous hydrogen, and in the absence of free oxygen, in contact with a catalyst capable of effecting the fixation of hydrogen to hydrocarbons, said catalyst being maintained at a temperature not materially below 600° C., and said vapors being maintained under pressure materially above atmospheric, thereafter allowing the products to expand into a separate expansion vessel, wherein the pressure is materially lower, and the speed of the gases is materially lower, than in the vessel containing the catalyst, whereby the bulk of the free carbon separates, and is deposited in said expansion vessel, and thereafter cooling the residual products, to produce by condensation, a liquid hydrocarbon containing less carbon than said relatively heavy hydrocarbon and especially adapted for use in high speed internal combustion engines.

2. The herein described method of converting relatively heavy hydrocarbons into lighter and more volatile hydrocarbons suitable for use in internal combustion engines, which process comprises vaporizing said relatively heavy

hydrocarbons alone, causing the vapors thereby produced, in the absence of extraneous hydrogen, and in the absence of free oxygen, to flow rapidly through a confined space under a pressure of several atmospheres, at a temperature sufficiently high to crack at least a portion of said hydrocarbon, in contact with a catalytic body, allowing the vapors so produced to expand into a separate expansion vessel, wherein the pressure is materially lower, than in the receptacle containing the catalytic body, and wherein the rate of flow of the vapors is lower than in the receptacle containing the catalytic body, whereby free carbon will be deposited in said expansion vessel, and thereafter cooling the vapors to condense liquid hydrocarbons.

3. The herein described method of converting relatively heavy liquid hydrocarbons into lighter and more volatile hydrocarbons adapted for use in high speed internal combustion engines, consisting in vaporizing the relatively heavy hydrocarbons, and subjecting the vapors under pressure, in the absence of extraneous hydrogen, and in the absence of free oxygen, to the action of a catalyst capable of effecting the fixation of hydrogen to hydrocarbons at a temperature sufficiently high to cause the separation of free carbon, allowing the products to expand into a separate [fol. 1188] expansion vessel, wherein a pressure is maintained, considerably lower than the pressure in the receptacle containing the catalyst, whereby the non-volatile materials are separated in said expansion vessel, and thereafter cooling the residual products, to produce by condensation, a liquid containing less carbon than the relatively heavy hydrocarbons employed.

4. In the treatment of hydrocarbons, of relatively high boiling points, for the production of hydrocarbons of lower boiling points, the step of passing a current of vaporized hydrocarbons, at a cracking temperature, and in the absence of extraneous hydrogen, in contact with a hydrogenating catalyst, under a pressure of several atmospheres.

5. The step of passing a current of hydrocarbon vapors under a pressure materially above atmospheric, in contact with a nickel catalyst, at a temperature sufficiently high to liberate free carbon, in the absence of extraneous hydrogen.

6. In the production of motor fuel from heavier hydrocarbons, the step of passing hydrocarbon vapors alone into contact with a catalytic, at a temperature above 600° C., under pressure materially above atmospheric.

7. The herein described method of converting relatively heavy liquid hydrocarbons into lighter and more volatile hydrocarbons, which comprises the step of vaporizing said relatively heavy hydrocarbons, and causing a current of the vapors to flow, in the absence of extraneous hydrogen, and in the absence of free oxygen, in contact with a catalyst capable of effecting the fixation of hydrogen to hydrocarbons, said catalyst being maintained at a temperature above about 600° C., and said vapors being maintained under pressure materially above atmospheric, thereafter allowing the products to expand into a separate expansion vessel, wherein the pressure is materially lower, and the speed of the gases is materially lower, than in the vessel containing the catalyst, passing the gases and vapors while at said lower pressure, through a device capable of removing free carbon, and thereafter cooling the residual products, to produce by condensation, a liquid hydrocarbon containing less carbon than said relatively heavy hydrocarbon and especially adapted for use in high speed internal combustion engines.

8. The herein described method of converting relatively heavy hydrocarbons into lighter and more volatile hydrocarbons, suitable for use in internal combustion engines, which process comprises vaporizing said relatively heavy hydrocarbons alone, causing the vapors thereby produced, without the addition of other gases or vapors, to flow rapidly through a confined space under superatmospheric pressure, and at a temperature sufficiently high to cause the liberation of free carbon, while in contact with a catalytic body, allowing the vapors so produced to expand into a separate expansion vessel, wherein the pressure is materially lower than in the receptacle containing the catalytic body, and wherein the rate of flow of the vapors is lower than in the receptacle containing the catalytic body, and passing the gases and vapors through a separating medium.

9. In the production of motor fuel, the step of suddenly lowering the pressure of a flowing mixture containing gases and vapors and containing suspended particles of free carbon carried by said mixture, while causing said gases and vapors to enter an expansion vessel, wherein the speed of flow of the gases and vapors is materially decreased.

10. A process of converting heavy hydrocarbon oils into hydrocarbons of lower boiling points which comprises passing the vapors of the hydrocarbons to be treated, under pressure materially above atmospheric and in the absence of steam, over a substance capable of producing a catalytic action, while maintaining said substance at a temperature approximating red heat.

11. A process of converting heavy petroleum oils into hydrocarbons of lower boiling points which comprises passing the vapors of the hydrocarbons to be treated, under superatmospheric pressure and in the absence of steam, over a hydrogenating catalyst while maintaining said catalyst at a temperature approximating a red heat.

12. A process of converting heavy hydrocarbon oils into hydrocarbon oils having lower boiling points, which comprises passing the vapors of said heavy hydrocarbon oils, under a pressure materially above atmospheric, and in the absence of steam, over a catalyst, while maintaining said catalyst at a temperature approximating a red heat.

13. In the manufacture of motor fuel from hydrocarbon oils of which at least portions have boiling points materially higher than those of ordinary gasolene, the herein described improvement which comprises passing such oil, in the form of a flowing current, in the substantial absence of extraneous water, through a coil maintained at a temperature not materially below 500° C., while at a pressure sufficiently low to allow vaporization, but materially above atmospheric, and thereafter rapidly lowering the pressure of the flowing mixture containing gases and vapors and containing suspended particles of free carbon carried by said mixture, and causing said gases and vapors to enter an expansion vessel, wherein the speed of flow of the gases and vapors is materially decreased.

14. A process of converting heavy hydrocarbon oils into [fol. 1189] hydrocarbons of lowering boiling points which comprises passing the vapors of the hydrocarbons to be treated, under a pressure of several atmospheres, in the absence of steam, over a metallic substance capable of producing a catalytic action, while maintaining said substance at a temperature capable of cracking the heavy oils.

15. A process of converting lamp oils or other hydrocarbons into hydrocarbons of lower boiling points, which comprises passing the vapors of the hydrocarbons to be treated, under a pressure of several atmospheres, over a catalytic metal maintained at a temperature at which said catalytic metal possesses catalytic activity.

16. A process of converting heavy hydrocarbons into hydrocarbons of lower boiling points which comprises passing the vapors of said hydrocarbons, under superatmospheric pressure and in the absence of steam or added hydrogen over a substance capable of producing a catalytic action, while maintained at a temperature capable of cracking oils.

17. A process of converting heavy hydrocarbons into hydrocarbons of lower boiling points, which comprises passing the vapors of said heavy hydrocarbons in the absence of steam or other extraneous hydrogen, under superatmospheric pressure, over a "catalytic body of the nickel type," at a temperature approximating a red heat, allowing the products of the reaction to expand to a lower pressure, and removing the solid materials from the vaporous products.

18. In the manufacture of motor fuel from hydrocarbon oils of which at least portions having boiling points materially higher than those of ordinary gasolene, the step of passing such an oil in the form of a flowing current, in the substantial absence of extraneous water, through a coil maintained at a temperature not materially below 500° C., while at a pressure sufficiently low to allow vaporization, but materially above atmospheric.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

William A. Hall.

Witnesses: Alfred S. Burbey, O. J. Worth.

[fol. 1190] PETITIONER'S EXHIBIT No. 181

C. S. PALMER.

PROCESS OF TREATING PETROLEUM RESIDUES.

APPLICATION FILED MAR. 2, 1907.

1,187,380. Patented June 13, 1916.

Fig 1

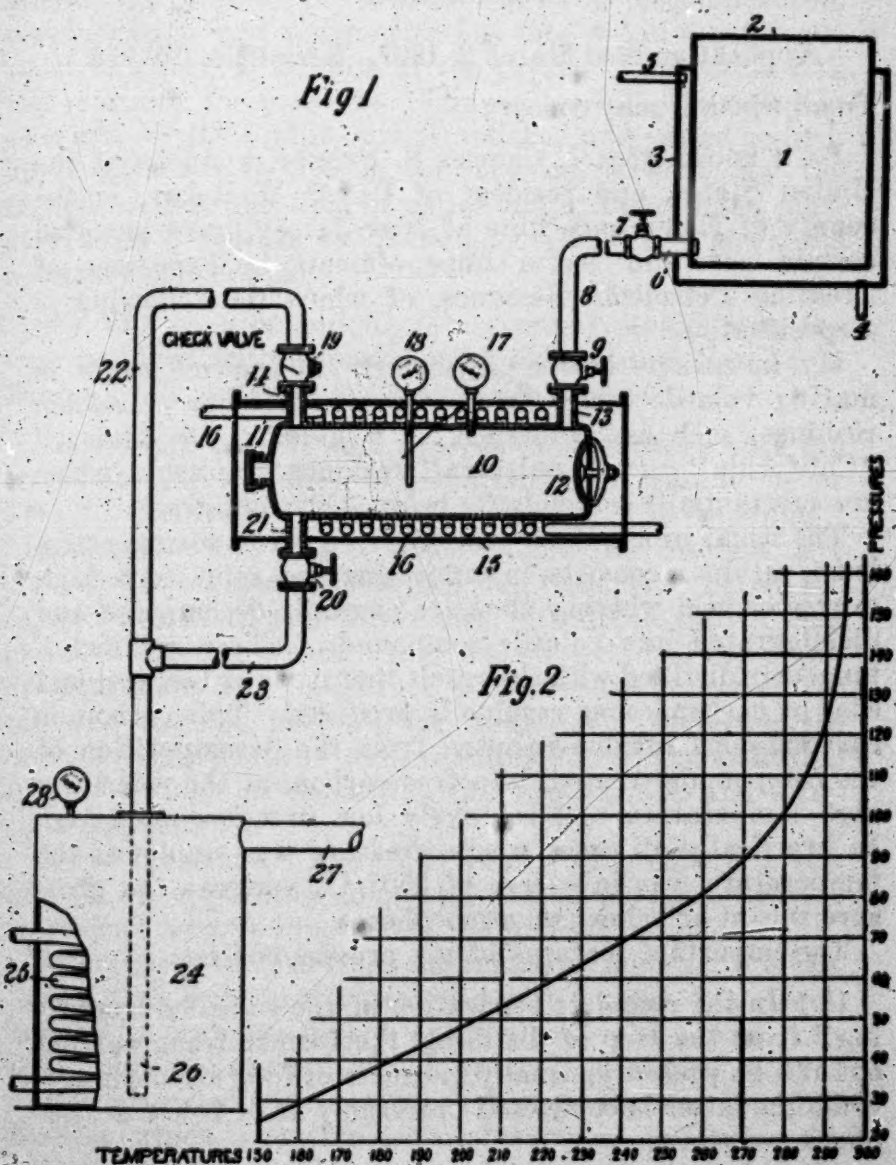


Fig. 2

Witnesses
Raphael Netter
H. D. Morrill

Inventor
Charles S. Palmer.
By his Attorneys
Byrnes, Townsend & Brownell

[fol. 1191] United States Patent Office

Charles S. Palmer, of Upper Montclair, New Jersey

Process of Treating Petroleum Residues

1,187,380. Specification of Letters Patent. Patented June 13, 1916

Application filed March 2, 1907. Serial No. 260,975

To all whom it may concern:

Be it known that I, Charles S. Palmer, a citizen of the United States, and resident of Upper Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Processes of Treating Petroleum Residues, of which the following is a specification.

My invention relates particularly to improvements in making volatile hydrocarbon compounds from petroleum residues, such as "Florence," "Boulder," "Wyoming," "California" and "Louisiana" residues or pitches which are substantially non-volatile below 300° centigrade.

The usual process of "cracking" or decomposing petroleum residues consists in subjecting the same to a high degree of heat whereby they are partially decomposed and disintegrated into volatile compounds. These are simultaneously distilled with the result that more or less residual coke or carbonaceous residue is produced. This carbon or carbonaceous residue resulted from the decomposition of the compounds treated, into free carbon, at the relatively high temperature and relatively low pressure employed. In practically all cases where pressure was employed the temperature was in excess of 350° C., whereas the pressure was at or below two atmospheres.

The important features of my process consist:

(1.) In the complete separation of the so-called "cracking" from the step of distilling, the former being carried out at high pressure, usually in excess of four atmospheres, while the latter is conducted preferably at or below atmospheric pressure.

(2.) In conducting the "cracking" in heavily constructed digesters capable of withstanding enormous pressures,

while supplying sufficient heat thereto to liquefy, to volatilize, to create a predetermined pressure, *i. e.* autogenous pressure, to furnish latent heat of volatilization, and to furnish the requisite endothermic heat of formation.

(3.) In utilizing the pressure element to direct and control the reaction quite contrary to usual expectations, the greater the pressure the greater will be the decomposition, recomposition and polymerization into volatile products, which are formed in spite of the pressure and work with and intensify the pressure. The pressure is controlled in each case by the equilibrium established and varies according to the materials treated, the resulting products, and the factors of heat and time of action but ordinarily the pressure when it reaches 130 pounds is sufficient to effect the necessary conversion.

(4.) The time of action. This usually, aside from the time required for the preliminary melting and heating in the reservoir, occupies but a very few minutes.

In carrying out the said process in accordance with my invention, the residues, substantially non-volatile below 300° C., such as "Florence," "Boulder," "Wyoming," "California" and "Louisiana" pitches or residues, are first introduced into a steam jacketed reservoir wherein the same are melted, and thence are introduced into a high pressure digester wherein they are subjected to the requisite conditions of temperature and pressure necessary for carrying out the process, the means for producing the requisite temperatures and pressures &c. Being indicated in the drawings accompanying this specification and forming a part thereof.

In the drawings, Figure 1 is an elevation chiefly in section of an apparatus adapted for this purpose. Fig. 2 represents a curve illustrating the process in operation.

Referring to the drawings the reference numeral 1, designates a tank or reservoir provided with a cover, 2, a steam-jacket 3, a drainage pipe 4, and a steam inlet pipe 5. An outlet pipe 6, provided with a valve 7, is connected by a pipe 8, provided with a valve 9, with a digester 10. The digester, which is constructed preferably of half-inch steel, is provided with a cap or closure 11, securely packed in the usual manner, a manhole 12, and pipe extensions 13, 14

and 21 respectively. A jacket 15 preferably as shown being provided with steam coils 16, completely surrounds the said digester, openings being provided in both the digester and the said jacket for the insertion of a pressure-gage 17 and a thermometer 18. The pipe-extensions 14 and 21 project through the jacket 15 and are provided with a check valve 19 and a stop-cock 20 respectively. These extensions are connected with piping 22 and 23 to a still 24, of well known construction, provided with the usual steam-coils 25, inlet and vapor outlet 27, and thermometer 28.

The residues treated in the above described apparatus, as actually practised, consisted in so far as could be determined from the specific gravity and melting points, of mix- [fol. 1192] tures of hydrocarbons of the paraffin series C_nH_{2n+2} of the range $C_{20}H_{42}$ to $C_{28}H_{58}$. Said residues are empirically known as residues or pitches from, as for example "Florence," "Wyoming," "California" and "Louisiana" pitches, which were the ones actually tested and operated on by this process.

During the treatment in the digester, 10, which usually did not exceed a few minutes, the pressures gradually increased with the temperature, according to the curve shown in Fig. 2, until a pressure of 130 pounds was reached, when there was apparently a sudden conversion of the materials present into more volatile compounds which caused a rapid increase in the pressures as shown without the indication of any great increase in temperature. Since the heat was being uniformly applied thereto, it is apparent that at this pressure there was a large absorption of heat, which prevented any noticeable indication of an increase in temperature. Such absorption of heat being evidently due to the formation of new compounds which as the results show are to a certain extent, at least, cyclic in character.

In order that the pressure may be accurately controlled during the operation, I provide the check valve 19, which may be adjusted for any degree of pressure desired, when upon an increase of the pressure above that to which the valve is set, the vapors from the digester will pass over into the still 24.

The steam heating coils are utilized in the apparatus for carrying out my invention in preference to other common heating means, because of the accuracy with which the tem-

perature can be adjusted, particularly if superheated steam is employed therein as is preferably the case.

The volatile products obtained from the above treatment, as actually carried out, were drawn off through the pipe 23 and collected in a still and subjected to distillation separately from the undecomposed residues remaining in said digester, at atmospheric pressure and upon fractional distillation gave results substantially as follows: Up to 100° C., about 5% distillate; between 100° C. and 150° C., about 10% to 20% distillate; between 150° C. and 200° C., about 10% to 20% distillate; between 200° C. and 250° C., about 20% to 30% distillate; between 250° C. and 300°C., about 10% distillate.

While the first fraction doubtless contained some volatile paraffin C_nH_{2n+2}, the higher distillates were mixtures of some paraffins, some benzenes C_6H_6, &c. and considerable naphthenes or "cyclic" or "closed ring" paraffins, such for example as polymethylenes, C_6H_{12}, and their homologues.

The materials which had been previously non-volatile below 300° C., after treatment uniformly yielded from 65% to 75% of volatile matters at temperatures varying from 100° C. to 300° C. Moreover, when the residues of one treatment were mixed with the residues of another batch or treatment, and were again treated there was no accumulation of none-volatile residue. In fact a non-volatile residue remaining from the last fraction of one treatment even if subsequently treated alone, would often be decomposed in a manner substantially similar to that of untreated residues when heated alone since each treatment would have its quota of undecomposed residue according to the equilibrium established. Accordingly, each residue when retreated would decompose exactly as though it had not been previously treated, as decomposition takes place at the appropriate equilibrium and long before all the residue is transformed.

In Fig. 2 the curve shown illustrates the process when operating up to 300° C. and the pressures ranging from 30 pounds up to 160 pounds, and in fact experiments show, that when operating even up to 400 pounds, the decomposition, recomposition and polymerization, other things being equal, is directly dependent upon the increase of pressure, and that the radical transformation into many

new compounds having new molecular arrangements, does not begin much below five or six atmospheres independent of the temperature. On the other hand, the said experiments indicate that at pressures ranging from 20 to 30 atmospheres the formation of new compounds takes place with great rapidity. In all cases the volatile products of decomposition increase with more pressure at temperatures from 200° 300° C. This indicates it is not merely the high temperature, but rather moderate temperature and high pressure that govern the decomposition and determine the result.

As a specific example: When operating with heavy, waxy, tarry or pitchy materials, such as "Florence," "Boulder," "Wyoming," "California" and "Louisiana" pitches, at temperatures ranging from 200° to 325° C. and under pressures of from 60 to 90 pounds, but a relatively small percentage approximating from 25% to 35% of volatile products were obtained. With temperatures from 200° up to 325° C. and pressures ranging from 100 to 150 pounds to the square inch, a large percentage of the originally non-volatile material treated was transformed into volatile compounds, the percentage ranging from 50% to 75% of the original. At pressures ranging from 150 pounds up to 300 and 400 pounds per square inch, and at temperatures of from 200° to 325° C., from 75% to 90% of the materials were converted into volatile products. These products were in all cases subjected to distillation, at, or below atmospheric pres- [fol. 1193] sure, separately from the digesting operation. Thus if one starts with a mixture consisting, for example, of paraffin of the C_nH_{2n+2} series it is obvious that if it is attempted to split up the said mixture into lighter molecules of the same series that there will be enough hydrogen to satisfy but a part of the possible new molecules that may be formed. The result will be the formation of compounds as C_nH_{2n}, or even C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{4n-6}, &c. Now these unsaturated, so to speak, possible compounds, might include the true unsaturated derivatives of the ethylene and cetylene series, although normally this is rarely the case, or of the benzene, toluene, naphthalene, anthracene, etc., groups which occasionally happens to be the case, or of the poly-methylene series, the naphthenes as di-, tri-,

tetra-, penta-, hexa-methylenes &c., and their derivatives, as is often and usually the case.

Throughout the claims the term "hydro-aromatic" as used, includes the cyclic and hydrobenzenes, including naphthenes and the poly-methylenes, the hydrobenzenes referred to being such compounds as $C_6H_6H_2$, $C_6H_6H_4$ and $C_6H_6H_6$.

The positive addition of catalytic materials, as originally described in this application, to the materials treated, is not claimed, as such, in this application, but is specifically reserved for a co-pending divisional application.

It is evident as herein described that the requisite pressure for effecting the transformation by decomposition, recomposition and polymerization of the residues treated into the desired volatile hydrocarbon compounds is created by and is directly dependent upon the temperature which is employed in the operation. Moreover, in view of the fact that the digester is sealed immediately after the introduction of the residues to be treated, it is evident that this pressure is created wholly without the introduction, and in the absence, of a foreign compressed gaseous medium.

Having thus described my invention, what I claim is:

1. The process of treating petroleum residues of the paraffin series to increase the yield of volatile compounds above that normally obtainable therefrom, which consists in digesting the same in a confined space under a pressure in excess of four atmospheres and not exceeding 400 pounds per square inch, said pressure being principally autogenous, and at a temperature in excess of 200° C., for a time sufficiently long to induce transformation of the major portion of said materials treated into more volatile products, said temperature being below that point at which sufficient carbonization occurs to substantially interfere with such transformation, and said digesting being conducted with the treated materials being continually subjected to the pressure throughout the said digesting period of the evolved volatilized compounds undiluted by added aqueous vapors.

2. The process of treating petroleum residues of the paraffin series to increase the yield of volatile compounds above that normally obtainable therefrom, which consists in digesting the same in a confined space under a pressure

in excess of eight atmospheres and not exceeding 400 pounds per square inch, said pressure being principally autogenous, and at a temperature in excess of 200° C., for a time sufficiently long to induce transformation of the major portion of said materials treated into more volatile products, said temperature being below that point at which sufficient carbonization occurs to substantially interfere with such transformation, and said digesting being conducted with the treated materials being continually subjected to the pressure throughout the said digesting period of the evolved volatilized compounds undiluted by added aqueous vapors.

3. The process of treating petroleum residues of the paraffin series to increase the yield of volatile compounds above that normally obtainable therefrom, which consists in digesting the same in a confined space under a pressure in excess of four atmospheres and not exceeding 400 pounds per square inch, said measure being principally autogenous, and at a temperature in excess of 200° C. for a time sufficiently long to induce transformation of the major portion of said materials treated into more volatile products, said temperature being below that point at which sufficient carbonization occurs to substantially interfere with such transformation, and said digesting being conducted with the treated materials being continually subjected to the pressure throughout the said digesting period of the evolved volatilized compounds undiluted by added aqueous vapors and then relieving said pressure and separating the evolved volatilized compounds from the non-volatilized compounds.

Signed at New York, in the county of New York and State of New York, this twenty-sixth day of February, A. D. 1907.

Charles S. Palmer.

Witnesses: W. H. Swenarton, Jas. H. Griffin.

[fol. 1194]

PETITIONER'S EXHIBIT 182

H. P. CHAMBERLAIN.

OBTAINING PRODUCTS FROM PETROLEUM BY DECOMPOSITION OF COMPONENT HYDROCARBONS THEREOF.

APPLICATION FILED OCT. 20, 1913.

1,221,790. Patented Apr. 3, 1917

Fig 1

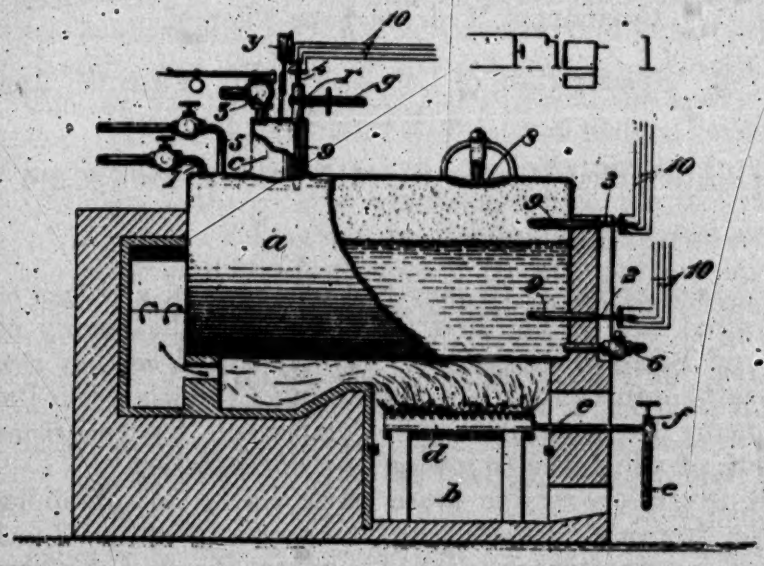


Fig 2.

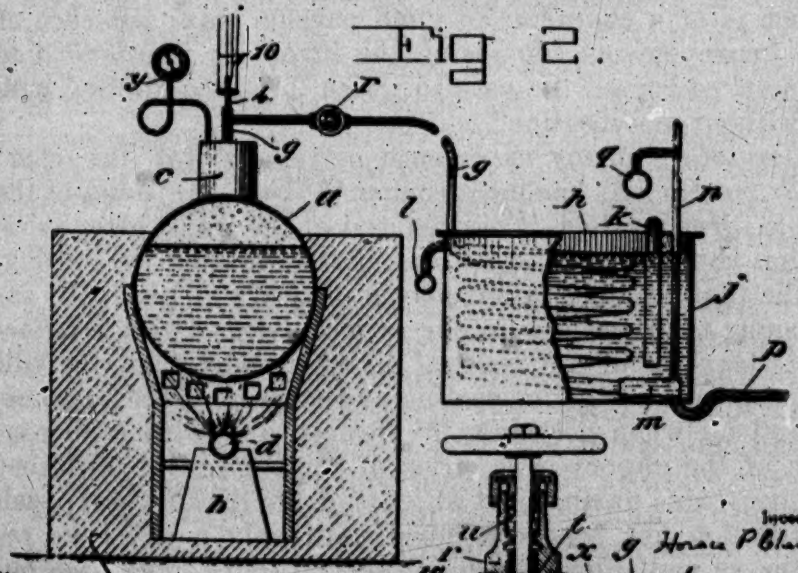
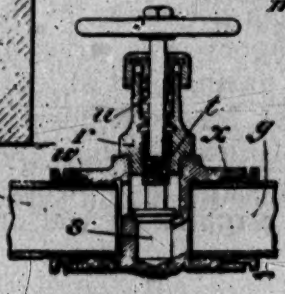


Fig. 3.



Inventor
Horace P. Chamberlain
by Chas. J. Hedlund
his Attorney

Witnesses
Percy Kay
F. W. Ernst

PX 197-1

[fol. 1195] United States Patent Office

Horace P. Chamberlain, of Buffalo, New York, Assignor to Standard Oil Company of New York, of New York, N. Y., a Corporation of New York

Obtaining Products from Petroleum by Decomposition of Component Hydrocarbons Thereof.

1,221,790. Specification of Letters Patent. Patented Apr. 3, 1917

Application filed October 20, 1913. Serial No. 796,310

To all whom it may concern:

Be it known that I, Horace P. Chamberlain, a citizen of the United States, residing at Buffalo, in the county of Erie and State of New York, have invented certain new and useful Improvements in Obtaining Products from Petroleum by Decomposition of Component Hydrocarbons Thereof, of which the following is a specification.

This invention relates more particularly to obtaining naphtha, burning oil (kerosene), an asphaltic material and another hereinafter mentioned product from petroleum which is of a character to yield paraffin wax; but each of the improvements composing the invention is intended to be secured for all the uses to which it can be applied with or without modification.

Heretofore in my experience petroleum (of the character mentioned) has most commonly been subjected in the crude form in which it is produced at the wells, after separation therefrom of water and earthy matter by settling, to distillation under atmospheric pressure at gradually increasing temperatures in one or more stills (with intermediate transfer of the residual oil when more than one still is used, with cooling or cooling and storage of the so transferred oil when necessary or desired and with condensation of the vapors in a series of condensers at different temperatures during part at least of the distillation); such distillation has been continued until only a dry coke remains as undistilled residue; and distillates have been obtained principally, if not exclusively, in the several forms (*a*) of crude naphtha in one or more grades, (*b*) water

white burning oil (kerosene) distillate, (*c*) mixed distillate which consists in part of hydrocarbons with boiling points normal for naphtha, in part of higher boiling hydrocarbons with viscosities normal for burning oil (kerosene), and in part of hydrocarbons with viscosities too great for normal constituents of burning oil (kerosene) and not great enough to be normal in other than light grades of lubricating oils, (*d*) heavy paraffin distillate, (*e*) heavy paraffin slop, and (*f*) crude still wax, also known as wax slop, as wax tailings or as gum. From the heavy paraffin slop and the crude still wax, an additional amount of heavy paraffin distillate has been obtained by further distillation of them. The points at which the different cuts (divisions or collections in different receivers) have been made have differed somewhat in different establishments and also at different times in the same establishments, owing to different views of the manufacturers as to the best methods of working, and so on, or to different market conditions. The normal boiling points of burning oil (kerosene) hydrocarbons have been recognized as between 302° F. and 572° F., or 518° F. (Allen, Commercial Organic Analysis, vol. 2, London, 1886, pages 397 and 398); as so defined, boiling points normal for naphtha would extend up to 302° F.; but for some years naphtha has included less volatile hydrocarbons; and for the purposes of the present specification volatility normal for naphtha should be taken to include boiling points up to 338° F. For the same purposes viscosities normal for burning oil (kerosene) hydrocarbons may be taken to extend up to seventy seconds at 100° F. by an Engler viscosimeter, on which water would exhibit a viscosity of fifty-three seconds at the same temperature; and the intermediate viscosities mentioned may be taken as from seventy to one hundred and seventy seconds by the same Engler instrument; which is also referred to whenever viscosity figures are given hereinafter.

With a view to increasing the yields of naphtha and burning oil (kerosene) hydrocarbons, it was long ago proposed to distil under superatmospheric pressure oils which are composed of or contain higher boiling hydrocarbons, as crude petroleum, for example, or undistilled residues of crude petroleum after removal therefrom of crude naphtha and water white burning oil (kerosene) distillate (with

or without obtaining more or less of the mixed distillate herein above mentioned). Such proposals seem to have little, if any, practical value; because, for one reason, distillation of crude petroleum and its undistilled residues under sufficient pressure could be carried on with safety in stills of practical size only to a comparatively slight extent on account of overheating the still bottoms. More recently it has been proposed to distil under superatmospheric pressure distillate oils composed of hydrocarbons with the intermediate viscosities mentioned, which for want [fol. 1196] of more profitable employment have commonly been disposed of as gas oil or fuel oil. They have been obtained in part as distillate in reducing (partially distilling) heavy paraffin distillate, from which paraffin wax has previously been separated by chilling and pressing, and also as residues (bottoms) in distilling the water white distillate and the mixed distillate already mentioned, respectively. So far as I am aware their component hydrocarbons have been (all or practically all of them) below and usually well below one hundred and seventy seconds in viscosity at 100° F. What practical use has been made of these proposals I am not sufficiently informed to state.

I have discovered that the entire heavy paraffin distillate obtained in the distillation of crude petroleum as aforesaid, treated with sulfuric acid and alkali, and retaining its content of paraffin wax, can be distilled under suitable superatmospheric pressure with the production of what may be called high pressure distillate yielding (by appropriate refining) a notable proportion of finished naphtha with boiling points up to 338° F. (more than I have obtained from high pressure distillate produced by distillating said gas oils or fuel oils under like conditions), and also a large proportion of refined burning oil (kerosene) of better quality than oil distilling over between the same limits of temperature, 338° F. to 518° F., which I have obtained from the high pressure distillate produced by distilling said gas oils or fuel oils under like conditions.

The burning oil (kerosene) from heavy paraffin distillate has been lighter in gravity and lower in viscosity than that from said gas oils or fuel oils and has also proved itself superior to the latter in burning tests, not exhibiting the same tendency as the latter to smoke, to produce a hard crust on the wick or to throw out mushroom-shaped

formations of carbon on the wick. This improved quality of burning oil (kerosene) is of special importance on account of the scarcity of high quality oil which could be used to mix with inferior oil in order to increase the yield of a desired standard.

The treatment of the heavy paraffin distillate with sulfuric acid and alkali and the presence therein of paraffin wax aid, each of them, in securing the results stated; but it is believed that advantage over the prior state of the art can be obtained without the aid of either of said features. Heavy paraffin distillate in each of four forms, that is to say, either pressed or unpressed and either treated or untreated with sulfuric acid and alkali, can be distilled under pressure in accordance with the invention, although not for all of said forms with the same advantage.

Such heavy paraffiin distillate in each of said forms contains liquid hydrocarbons with viscosities normal to heavy and medium grades of lubricating oils and also hydrocarbons with the intermediate viscosities mentioned in such relative proportions that in the distillation under pressure the decomposition of the hydrocarbons of each of said kinds is modified by the presence of the two other kinds. For exerting such modifying effect the hydrocarbons of any of said kinds should not be less than about ten per cent. by volume of the sum total of the three kinds; and in the distillate mentioned the kind present in least proportion is in excess of such ten per cent. Said distillate is also so far free from still wax and like heavy matters of sticky character and from elements yielding the same or coke that charges of the said distillate of practical size can be distilled under a superatmospheric pressure of seventy five pounds to the square inch to the extent of fifty per cent. or more by volume without heating the still bottom to redness. I have also discovered that certain advantages over the prior state of the art can be obtained by distilling as aforesaid oils related to heavy paraffin distillate as hereinafter explained.

In yielding naphtha and burning oil (kerosene) the decomposed hydrocarbons may yield also a residual product of an asphaltic character which is useful and I believe new and which is included in the invention as a new article of manufacture or composition of matter.

I have also discovered I believe a new process of distilling hydrocarbon oils under superatmospheric pressure; which I have applied to heavy paraffin distillate in each of the forms mentioned; but which I believe can be applied advantageously (as compared with the prior state of the art) to other forms of petroleum (including crude oil and undistilled residues in case it should be found expedient to distil the same under superatmospheric pressure, as well as the herein above mentioned gas oils or fuel oils and other distilled or partly distilled products), and also to hydrocarbon oils from other sources than petroleum.

I have also devised a distilling apparatus which is useful for performing said process and which I believe to be new and consequently regard as forming part of the present invention.

The accompanying drawings represent by way of example an apparatus within the invention, Figure 1 being a longitudinal vertical section, partly in elevation, of the still and accessories, without the condenser, Fig. 2 a view in cross section, partly in elevation, showing still and condenser, and Fig. 3 a detail view in section on an enlarged scale of an expansion valve appropriate to be employed as a vapor throttling device in said apparatus.

[fol. 1197] The still *a* is advantageously of box-like form and of a large enough capacity to be of practical value in industrial use, say a horizontally disposed cylinder eight feet in diameter and eighteen to thirty feet in length, or of other appropriate dimensions. It is supported above a fireplace *b* for heating and has its upper portion exposed to the atmosphere with little or no protection against cooling. It is best provided with a dome *c* also exposed to the atmosphere. The heating means may be of any appropriate description. A burner *d* is shown by way of example, the same having a gas supply pipe *e* connected therewith and provided with a controlling valve *f*. Any desired number of burners can be used; also one or more fires burning solid or liquid fuel can be used in connection with supplementary gas burners; or other heating arrangements can be adopted. The still, when its bottom becomes heated to incipient redness (the ordinary indication of danger to a still bottom from overheating should distillation be continued) ought then to be able to withstand an internal pressure in such excess of eighty pounds per

square inch above atmospheric pressure as to afford a proper margin of safety.

The intermediate section of the still (see Fig. 2) is *is* best protected both from the atmosphere and from the fire gases, the cubic contents of the so protected portion being not less than about half the capacity of the still. As shown, about a third of the exterior surface of the still is exposed to the atmosphere, approximately another third is exposed to the fire gases, and the remaining portion, approximately one-sixth on each side, is inclosed by and in contact with the walls of the still setting and is so protected thereby both from the atmosphere and from the fire gases.

The vapor pipe *g* leads from dome *c* to a condenser of any known or suitable form; shown as a coil *h* immersed in a tank *j*. Water of a temperature to condense naphtha and heavier vapors is supplied to tank *j* by water inlet pipe *k* and withdrawn therefrom in a warmer state by water outlet pipe *l*. At *m* within tank *j* is a gas separating box with a gas escape pipe *n* leading from its top and a distillate outlet pipe *p* leading from the bottom to a receiver (not shown). At *q* is a gas main for carrying away the gas to be burned. Additional fuel would, of course, be needed for heating the still *a* in case gas from the same should be burned under it.

The vapor pipe *g* is provided with an expansion valve *r* intermediate the dome *c* of still *a* and the condenser. As the best conduct of the pressure distillation requires a close regulation of the volume of escaping vapors, the valve port *s* (Fig. 3) is best of small size as compared with the bore of vapor pipe *g*; which bore should not be less than about three inches in diameter in order to avoid difficulty from choking. As shown, the valve is closed by a screw *t* and has a stuffing box *u* for its stem. Stuffing boxes are also shown at *w* and *x* for the pipe connections.

The valve shown is a form known on the market as of needle type and employed (for one purpose at least) as an expansion valve in ice machines using liquefied ammonia as the refrigerating agent. A valve of more pronounced needle form (more acute taper and further projection into the port) might have advantages; but the form shown has been found useful. A valve of other than needle type is not necessarily excluded. Heretofore in plans for

distilling petroleum and other hydrocarbons oils under superatmospheric pressure it has been proposed to employ a relief valve which rises automatically when the pressure reaches a certain degree and closes when the pressure falls below the same degree. The use of such automatic valve is not necessarily excluded; but its use is attended with no advantage, in my opinion; while, on the other hand, it adds complication to the apparatus and is liable to cause danger or inconvenience by sticking. If used, it would be advantageous to provide means for manually regulating the extent of the valve's opening and for forcing it positively to and from its seat, should occasion arise.

The still is shown provided with a pressure gage *y* for exhibiting the pressure inside the still, a safety valve *z* for relieving said pressure should it accidentally become excessive, a pyrometer 2 for exhibiting the temperature of the oil in distillation, a second pyrometer 3 for exhibiting the temperature of the vapors in the vapor space at the front of the still, a third pyrometer 4 for exhibiting the temperature of the vapors as they leave the dome *c* and pass over to be condensed as distillate, a valved oil supply pipe 5, a valved discharge pipe 6 for the residual product, a steam pipe 7 for introducing steam at the close of each run in order to expel hydrocarbon vapors and to cool the still off more rapidly, and a manhole 8 for cleaning out the still at the end of each run. Each pyrometer is inclosed in a protecting sheath or pipe 9 closed at the inner end. Electric pyrometers with wires 10 are indicated.

For obtaining the oil to be supplied to still *a* crude petroleum may well be distilled to dryness under atmospheric pressure in one or more externally heated stills (not shown) with gradual rise of temperature and with fractional condensation of the vapors in the latter part at least of the run, customary apparatus being used for the purpose. [fol. 1198] After the collection of the water white burning oil (kerosene) distillate and of such amount of the mixed distillate coming over subsequently as may be desired, the distillate which is subsequently received in such distillation may well be collected in the receiver for heavy paraffin distillate as long as it is sufficiently free from still wax to be readily pressed for paraffin wax. Assuming that the crude oil operated upon is from the Kansas oil fields and has itself a specific gravity of 0.863, such collection may

well include all the distillate which at the condenser outlet is between 0.855 and 0.904 in specific gravity at 60° F.

Distillate which is received afterward in said distillation of the crude oil may well be itself distilled to dryness, and the so obtained distillate, so long as it is free from still wax, be added to the heavy paraffin distillate of the crude oil run.

The thus obtained material would best be treated with sulfuric acid and alkali in the manner customary for treating heavy parafin distillate therewith preparatory to chilling and pressing, to wit, by agitation with them in succession and by separation of the resulting sludge after each agitation. So treated, and with its content of paraffin wax intact, it would constitute heavy paraffin distillate in the form in which it is considered best to employ the same for decomposition in the still *a*.

It would consist principally of hydrocarbons, which (if separate) would be liquid at 60° F.; but it would also contain over four per cent. by volume of paraffin wax (in solution). Its liquid portion would comprise hydrocarbons with viscosities normal to medium grades of lubricants (to wit, from one hundred and seventy seconds to two hundred and ninety seven seconds) and also hydrocarbons with viscosities normal to heavy grades of lubricants (to wit, from two hundred and ninety seven seconds upward) as well as hydrocarbons whose viscosities lie between those normal to burning oil (kerosene) and those normal to medium lubricants (to wit, between seventy seconds and one hundred and seventy seconds). Each of these species of liquid hydrocarbons would be present in above 10 per cent. by volume. A sample from a particular lot of treated and unpressed heavy paraffin distillate which had as a whole a specific gravity of 0.881 at 60° F. and whose distillation under pressure gave results hereinafter set forth was chilled and pressed for paraffin wax and yielded the latter at the rate of sixteen and a half pounds to each 42-gallon barrel of the unpressed distillate (equivalent to six per cent. by volume). The so pressed sample was then reduced with free superheated steam introduced into the oil and with fractional condensation of vapors in a series of condensers at different temperatures in the manner customary in obtaining lubricating oils (light and medium grades as distillates and

heavy grades as residues) from pressed paraffin distillate and in such reduction yielded (1) distillate with viscosities at the condenser outlet up to seventy seconds equal to one per cent. by volume of the unpressed distillate, (2) distillate with viscosities at the condenser outlet between seventy seconds and one hundred and seventy seconds equal to fifty six 44/100 per cent. thereof, and (3) distillate with viscosities at the condenser outlet between one hundred and seventy seconds and two hundred and ninety seven seconds equal to thirteen 89/100 per cent. thereof, leaving (4) residual oil equal to twenty 38/100 per cent. thereof. There was thus an estimated loss of two 29/100 per cent. by volume in the assay.

The treated and unpressed heavy paraffin distillate is introduced through pipe 5 into the still *a* until the latter is say six-tenths full. The contents of the still are then gradually raised in temperature, with valve *r* open, until the air has been expelled from the still and oil appears as condensate at the condenser outlet. Next the valve *r* is closed and the pressure in the still *a* is allowed to accumulate until the gage *y* shows say 75 pounds per square inch above atmospheric pressure. Thereupon the valve *r* is cautiously opened; and the heating is carefully regulated to maintain said pressure of 75 pounds without greatly exceeding it. The extent to which the valve *r* is opened is an important matter. It may well be opened to such extent that distillate is received from the condenser *b* at the rate of about two per cent. by volume of the original charge per hour of running. It may be opened to a lesser extent, as much less as may be desired; since the only objection to the resultant slower running would be the increased expense due to the longer time to make the run. It may be opened to a greater extent; but with too large an opening excessive firing would be necessary to maintain a proper pressure in the still *a*; and, in consequence of such firing, the hydrocarbons passing over might average too high in specific gravity for profitable working. A general increase of as much as twenty four one thousands (0.024) in the specific gravity of the high pressure distillate (as compared with that obtained in a distillation of oil from the same lot at the said two per cent. per hour rate) would probably indicate a fatal impairment in the quality of high pressure distillate. Such

comparison should be made between samples to be collected at corresponding periods of the runs, to wit, when the distillate received in each run shall be the same percentage of the original charge.

[fol. 1199] The valve *r* can be adjusted during a run, if considered necessary or expedient, but in normal running the valve opening may be constantly established, so as to allow a continuous escape of the vapors through it; and it need not be altered in size, thus allowing an approximately uniform escape of vapors with an approximately uniform pressure in the still.

As distillation proceeds, the oil in distillation becomes gradually hotter. Its temperatures will be higher than those of the oil in a parallel run under atmospheric pressure; but they may be (and in distilling heavy paraffin distillates under a pressure of seventy five pounds have been found to be) below those at which the vapor tension of the undecomposed oil is estimated to equal the still pressure on the basis of considering the rise in vapor tension of the undecomposed oil for a given number of degrees F. above its boiling point to be equal (or sufficiently near equal) to the rise in vapor tension of benzene (coal tar naphtha, C_6H_6) for an equal number of degrees F. above its boiling point and the temperatures of the oil in distillation in a parallel run under atmospheric pressures to represent (with sufficient accuracy) the boiling points of the undecomposed oil. Hereinafter a table is given which shows the temperatures of the oil in parallel runs on heavy paraffin distillate under atmospheric pressure and under seventy five pounds superatmospheric respectively; and it will be observed by reference thereto that at corresponding periods of the runs the difference is less than 131° F.; which is the difference in temperature between benzene at its boiling point (where its vapor tension equals the pressure of the atmosphere) and at the point where its vapor tension is seventy five pounds to the square inch above atmospheric pressure.

The evolved vapors are cooled in the exposed upper part of still *a* and in dome *c* to considerable extent (say between about 150° F. and about 350° F. below the contemporaneous temperatures of the oil in distillation) before they pass over to be condensed as distillate. Such cooling results in a partial condensation of said vapors and the formation

of condensate which returns to the oil in distillation. It is conceived that some hydrocarbon components of the oil in still *a* will vaporize without decomposition, owing to the presence in the still *a* of the vapors of lighter (more volatile) hydrocarbons formed by decomposition, notwithstanding the fact that the temperature of the oil in distillation is below the estimated boiling point of the latter under the pressure in the still *a*.

The following table gives figures which were obtained in runs performed at the rates indicated in the table with a small still (a horizontal cylinder 20 inches in diameter by 42 inches long with a dome four inches in diameter and six inches high) on batches from the same lot of oil, one under atmospheric pressure and the other under a super-atmospheric pressure as near 75 pounds to the square inch as practicable without falling below the same. The total hours and minutes of performing the respective runs, in connection with the total percentages received therein, show average yields of distillate equal to about seven and a half per cent. by volume of the original charge per hour in one run and about eight per cent. per hour in the other; but in industrial operations a lesser rate is considered better as hereinabove indicated.

The specific gravities in the table are those of the several fractions of distillate of 5% each by weight; and the times in minutes are those in which said fractions were severally received.

Fractions 5% each.	Atmospheric pressure. Liquid oil, degrees F.	Vapors in dome, degrees F.	Specific gravity.	Time, minutes.	75 pounds gage pressure. Liquid oil, degrees F.	Vapors in dome, degrees F.	Specific gravity.	Time, minutes.
1	663	588	.8236	40	766	512	.7669	48
2	679	582	.8473	43	756	520	.7673	43
3	691	624	.8529	45	766	525	.7682	46
4	701	635	.8536	38	769	530	.7762	35
5	710	635	.8581	40	775	529	.7770	37
6	715	658	.8540	43	778	530	.7758	41
7	722	656	.8571	41	777	535	.7809	38
8	734	676	.8560	40	782	540	.7818	41
9	740	680	.8555	44	793	545	.7844	46
10	741	635	.8473	43	804	550	.7945	37
11	752	655	.8519	40	811	554	.7967	38
12	760	688	.8514	38	815	546	.8053	36
13	765	691	.8524	39	834	550	.8170	40
14	770	696	.8534	45	842	546	.8299	50

Total distillate 70%; time 9 h. 39 m.; total distillate 70%; time 9 h. 36 m.

Percentages in table by weight, not volume; total distillate 72% by volume in run under atmospheric pressure, and 78.2% by volume in run under 75 pounds gage pressure.

In giving these and other figures in detail, it will be understood that they are by way of example only, in order the better to enable those skilled in the art to practice the invention.

[fol. 1200] It is considered best in distilling under pressure that the evolved vapors should not be heated above the contemporaneous temperatures of the oil in distillation. As shown, therefore, only the bottom third or thereabout of the exterior surface of the still is exposed to the fire gases; so that the walls of the vapor space, even when this space is enlarged by progress of the distillation, will not be exposed thereto. The cooling of the vapors is effected as shown by the exposure of the still top and dome to the cooling influence of the atmosphere. The work performed by

the vapors in expanding as they pass the valve *r* in distillation under high pressure, with said valve within a short distance from dome *c*, also exerts a cooling effect on the vapors in said dome *c*. The condensate as formed drops (or else runs down the sides of the still) into the oil in distillation. A partial condenser exteriorly located and connected with the still by a vapor pipe and a run back for returning condensate could be used instead of or in addition to cooling in the vapor space (including dome space when a dome is used).

By having the middle section of the still inclosed by and in contact with the walls of the still setting, the vapors are protected not only against overheating, as just mentioned, but also against the undue cooling which might result from enlargement of the vapor space during the run, were said middle section exposed to the atmosphere.

The distillation would best be continued as long as it is safe to do so, in view of the superatmospheric pressure in the still. The limit of safety would probably be about reached when the appearance of the still bottom indicates incipient redness.

The run being thereupon terminated, the asphaltic material in the still *a* is withdrawn through pipe 6 and a cooler (not shown) into an appropriate receiver (not shown); the still is subsequently cooled (after introduction of free steam through pipe 7 to expel the vapors, the manhole 8 being opened as the steam first enters); the still is cleaned; and it is then ready to receive a new charge of the treated unpressed heavy paraffin distillate.

The high pressure distillate from condenser coil *h* may well be collected in a single receiver (none shown) and be then fractionated into naphtha, burning oil (kerosene) and a heavier oil useful as gas or fuel oil. Said heavier oil, also any residue obtained in rerunning the burning oil (kerosene) portion of the high pressure distillate, could be added in whole or in part to a new charge of the heavy paraffin distillate, if so preferred. Other oils could also be added, if so desired such as residues (bottoms) from rerunning the water white distillate and the mixed distillate of the crude oil run. Instead of a single condenser *h* as shown, a series of condensers maintained at different temperatures could be applied to the pressure still *a*.

The asphaltic residual material withdrawn from the still *a* at the close of the high pressure run in which the figures of the table were obtained had as a whole a specific gravity of 1.0772, and was as a whole ninety eight 65/100 per cent. soluble in carbon bisulfid and eighty two 95/100 per cent. soluble in naphtha obtained from Kansas crude oil and consisting of hydrocarbons with specific gravities ranging from 0.7526 to 0.7692.

If so desired, the pressure distillation can be arrested before the material in the still attains the specific gravity mentioned. Also, if so desired, further distillation can be carried on under atmospheric or other reduced pressure, with or without introduction of free superheated steam or other aeriform fluid (including atmospheric air, should it be desired to modify the composition by oxidation). As obtained from the high pressure still the asphaltic material will ordinarily be soft and sticky even at zero F., on account of the conduct of the distillation only while it can be carried on with safety; but by reduction (partial evaporation) under atmospheric pressure at appropriately high temperature and with introduction of superheated steam into the melted material, it can be brought to such condition that when cool a lump of the same can be molded and drawn out into threads. Distillate obtained from such reduction can be added to heavy paraffin distillate to be distilled under the high pressure mentioned; it could be used as gas oil or fuel oil; or it could be otherwise disposed of, as preferred.

The solution of the asphaltic material as obtained from the high pressure still in the naphtha mentioned (in such proportions as to give the desired fluidity for application) constitutes an excellent varnish or protective coating. The material can be so dissolved and used after reduction (partial evaporation) and oxidation (either or both). It can be used also (alone or in connection with asphaltum and with or without reduction and oxidation, either or both, as may be necessary or expedient) for paving and roofing purposes and for other purposes to which asphaltum has been applied.

While it is considered best to charge the pressure still with an oil which represents an entire range of hydrocarbons from and including some with the intermediate viscosities mentioned to and including those recovered from

heavy paraffin slop, more or less of said hydrocarbons can be collected separately, if so preferred, and only the remainder of them charged into the still.

[fol. 1201] It is also permissible within the limits of the invention as expressed in one or more claims to make artificial mixtures of hydrocarbons with the intermediate viscosities and those with viscosities normal to lubricating oils of (either or both) medium and heavy grades, the words "artificial mixtures" being used in opposition to a natural mixture of said kinds of hydrocarbons such as exist, for example, in heavy paraffin distillate obtained as aforesaid.

Also oil composed of or containing hydrocarbons with the intermediate viscosities mentioned can be enriched with paraffin wax or an appropriate substitute artificially, or by collecting a distillate containing paraffin wax.

Yet further within the limits of the invention oil containing liquid hydrocarbons with viscosities normal to medium and heavy lubricating oils (either or both) and oil containing hydrocarbons with the intermediate viscosities mentioned can be distilled separately under pressure and the resulting products can then be mixed. In this way burning oil (kerosene) from distilling oil of the latter kind under pressure can be improved by the better quality of that from distilling oil of the former kind. I have obtained larger yields, however, both of naphtha and of burning oil (kerosene) from distilling mixtures of (1) hydrocarbons with viscosities normal to heavy lubricating oils and (2) hydrocarbons with the intermediate viscosities mentioned than from distilling like volumes of said two kinds of liquid hydrocarbons separately; and I believe that the same principle would hold true in respect to mixtures containing hydrocarbons with viscosities normal to medium lubricating oils. It is also my belief that better results are attainable by distilling oil in which two or more of said three kinds of liquid hydrocarbons are naturally present than by separating such hydrocarbons and then forming a mixture artificially of them in their original proportions.

In making heavy paraffin distillate a certain amount of decomposition is considered necessary in order to form crystallizable paraffin wax. It is provoked by introducing little or no inert aeriform fluid (like superheated steam) into the still and by cooling the evolved vapors sufficiently

to form a condensate which is returned to the oil in distillation. The cracking customary in making heavy paraffin distillate is considered advantageous where such distillate is to be subjected to pressure distillation, for one reason because it removes from the distillate certain coke forming elements; and, if preferred, it can be carried further in preparing distillate for subsequent pressure distillation than is customary in preparing heavy paraffin distillate. On the other hand, it need not necessarily be carried to this extent or to any avoidable extent within the limits of the invention as expressed in some at least of the claims. Aeriform fluid, such as superheated steam, could, for example, be introduced into crude petroleum in preparing a distillate to be itself distilled under superatmospheric pressure.

In the pressure distillation it is considered best, as mentioned herein above, to use about 75 pounds to the square inch above atmospheric pressure. Above this pressure the yields of naphtha and burning oil have not been found by me to increase (rather the reverse); while, of course, the danger increases with the pressure. Below 75 pounds pressure I have found the yields to fall off gradually with the diminution of pressure; so that under 30 pounds the yield of naphtha has been about three-fifths and under 20 pounds less than half of the yield under 75 pounds; while the yield of burning oil (kerosene) under 30 pounds has been about four-fifths and under 20 pounds less than three-fourths of the yield under 75 pounds. In order that, in a run under 30 pounds, the temperatures of the oil in distillation may not be as high as those at which the vapor tension of the undecomposed oil is estimated to equal the still pressure, said temperatures should not be so much as about 73° F. above the temperatures attained at corresponding periods in a parallel run under atmospheric pressure. In runs under a pressure other than 30 pounds and 75 pounds, the temperatures of the oil in distillation should be within a corresponding maximum above the so attained temperatures in order that they may be less than those at which the vapor tension of the undecomposed oil is estimated to equal the still pressure. The vapor tensions of benzene (C_6H_6) are known for a wide range of temperatures. Such tension amounts to 30 pounds superatmospheric at about 73° F. above the boiling point, to wit, at about 250° F., the boiling point of benzene being about 177° F.

The application of the invention, or of applicable portions thereof, to petroleum not of a characer to yield paraffin wax and to hydrocarbon oils other than petroleum will be sufficiently evident from the preceding description. There may well be petroleum which does not yield paraffin wax, but which does yield distillate composed of liquid hydrocarbons divisible by their respective viscosities into the three kinds mentioned; and there may well be petroleum which does not yield distillate having hydrocarbons so divisible; but all crude petroleum can be distilled to dryness under a suitably low pressure and with or without designedly provoked cracking in order to obtain distillate [fol. 1202] to be decomposed by distillation under high pressure, which distillate may contain at least the higher boiling hydrocarbons yielded by such petroleum down to but excluding last runnings that would be objectionable by reason of the presence therein of still wax or like heavy matters of sticky character, but not necessarily excluding desirable hydrocarbons recoverable by the rerunning of slops.

Instead of relieving the vapors (to wit, at valve *r*) from the high pressure under which they are evolved in a still *a* prior to their condensation (to wit, in condenser *h*), they can be held under said pressure (to wit, by appropriate provisions, not shown, such as valves, for example, in pipes *n* and *p*) until condensed as distillate without thereby necessarily discarding all the new, useful and original features of the present invention. Either way the contents of the still would be confined in order to develop therein the superatmospheric pressure mentioned.

Working on the continuous system (in which a more or less continuous stream of oil is supplied to a high pressure still and a like stream of residuum withdrawn therefrom during the progress of the distillation) is not necessarily excluded from the scope of the present invention; although it is considered more advantageous to work by the batch system, as herein above described (in which a charge of oil is supplied to still *a* and then run off to the desired extent, the still being thereupon emptied preparatory to receiving a new charge).

The mention of particular modifications is not intended to exclude others not mentioned in which the substance of one

or more of the hereinafter written claims may be embodied.

In reciting in claims following that the oil is "free from still wax and like heavy matters of sticky character and from elements yielding the same or coke," a practical rather than a theoretically perfect freedom is to be understood. It suffices, for example, for the oil operated upon to be distillable in an externally heated still of the dimensions hereinbefore mentioned for still *a* (charged six-tenths full) under a super-atmospheric pressure of seventy five pounds to the square inch at the aforesaid rate of two per cent. per hour to the extent of fifty per cent. or more by volume of its component hydrocarbons which have viscosities above seventy seconds at 100° F. without heating the still bottom to redness.

I claim as my invention or discovery:

1. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in operating upon an oil that contains hydrocarbons with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. and also liquid hydrocarbons with higher viscosities in the relative proportions of not less than ten per cent. by volume of hydrocarbons of either kind to not exceeding ninety per cent. of hydrocarbons of the other kind and that is free from still wax and like heavy matters of sticky character and from elements yielding the same or coke by distilling such oil at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds per square inch, substantially as described.

2. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in operating upon an oil that contains paraffin wax and also liquid hydrocarbons with viscosities too great for normal constituents of burning oil (kerosene) in the relative proportions of not less than four nor more than ninety per cent of paraffin wax to not more than ninety-six per cent. nor less than ten per cent. of said liquid hydrocarbons and that is free from still wax and like heavy matters of sticky character and from elements yielding the same or coke by distilling such oil at decomposing temperatures under a super-

atmospheric pressure of not less than thirty pounds per square inch, substantially as described.

3. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in subjecting to distillation at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds per square inch the heavy paraffin distillate which is collectable in an appropriate distillation of crude petroleum of a character to yield paraffin wax, which is free from still wax and like heavy matters of sticky character and from elements yielding the same or coke, and which consists of hydrocarbons with viscosities ranging from below one hundred and seventy seconds at 100° F., to above two hundred and ninety-seven seconds at 100° F., upward of ten per cent. by volume of said hydrocarbons having viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F., substantially as described.

4. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in distilling crude petroleum approximately to the point at which the distillate would no longer be free from still wax or like heavy matters of sticky character, collecting distillate up to this point from a point so early in the run that hydrocarbons with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. represent upward of ten per cent. by volume of the so collected distillate, and subjecting the so collected distillate to distillation at decomposing temperatures under a superatmospheric [fol. 1203] pressure of not less than thirty pounds per square inch, substantially as described.

5. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in distilling crude petroleum approximately at least to dryness, collecting distillate in such complete distillation in distinct portions, one of them containing the runnings to approximately the point at which the so collected distillate would be no longer free from still wax and like heavy matters of sticky character from a point so early in the run that hydrocarbons with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F.

represent upward of ten per cent. by volume of the so collected distillate, and the other of them comprising the subsequent runnings, distilling these subsequent runnings approximately at least to dryness with collection by itself of distillate free from still wax and like heavy matters of sticky character, mixing this latter distillate with said first portion of distillate from the crude oil run, and subjecting the mixed distillates to distillation at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds per square inch, substantially as described.

6. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in obtaining oil that consists of a natural mixture of hydrocarbons with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. and hydrocarbons with higher viscosities including those above two hundred and ninety seven seconds at 100° F. in the relative proportions of not less than ten per cent. by volume of hydrocarbons of either kind to not exceeding ninety per cent. of hydrocarbons of the other kind and that is free from still wax and like heavy matters of sticky character and from elements yielding the same or coke, and distilling such oil at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds per square inch, substantially as described.

7. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in distilling at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds to the square inch, hydrocarbons that have viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. and that are free from still wax and like heavy matters of sticky character and from elements yielding the same or coke and in also distilling at decomposing temperatures under said superatmospheric pressure liquid hydrocarbons that have viscosities above one hundred and seventy seconds at 100° F. and that are similarly free from said matters and elements, and uniting hydrocarbons given off as vapors in such distillation from said two kinds of parent hydrocarbons in the relative proportions of not less than

ten per cent. by volume of product from either kind to not exceeding ninety per cent. of product from the other kind, substantially as described.

8. The process of obtaining hydrocarbon products by decomposition of hydrocarbons, which process consists in distilling at decomposing temperatures under a superatmospheric pressure of not less than thirty pounds to the square inch, paraffin wax in a form that is free from still wax and like heavy matters of a sticky character and from elements yielding the same or coke and in also distilling at decomposing temperatures under said superatmospheric pressure liquid hydrocarbons that have viscosities too great for burning oil (kerosene) and that are free from still wax and like heavy matters of a sticky character and from elements yielding the same or coke, and uniting hydrocarbons given off as vapors in such distillation from said paraffin wax and said liquid hydrocarbons in the relative proportions of not less than four nor more than ninety per cent. by volume of product from said paraffin wax to not more than ninety-six per cent. nor less than ten per cent. of product from said liquid hydrocarbons, substantially as described.

9. An asphaltic material for varnish making and other uses, the same being as a whole more than ninety per cent. by volume soluble in bisulfid of carbon and more than seventy five per cent. soluble in petroleum naphtha, and consisting over fifty per cent. of hydrocarbons that are heavier than water and are of a coherent and ductile character and that are residues of the decomposition of hydrocarbons with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. and also of liquid hydrocarbons with higher viscosities in the relative proportions of not less than ten per cent. by volume of product from hydrocarbons of either kind to not exceeding ninety per cent. of product from hydrocarbons of the other kind, substantially as described.

10. An asphaltic material for varnish making and other uses, the same being as a whole more than ninety per cent. by volume soluble in bisulfid of carbon and more than seventy five per cent. soluble in petroleum naphtha, and consisting over fifty per cent. of hydrocarbons that are heavier

than water and are of a coherent and ductile character and that are residues of the decomposition of paraffin wax and also of liquid hydrocarbons with viscosities too great for normal constituents of burning oil (kerosene) in the [fol. 1204] relative proportions of not less than four nor more than ninety per cent. of product from paraffin wax to not more than ninety six nor less than ten per cent. of product from said liquid hydrocarbons, substantially as described.

11. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form to temperatures sufficient to effect decomposition of the oil under a superatmospheric pressure of not less than thirty pounds per square inch, when the still contents are suitably confined, (2) conducting the evolved vapors to condensing means through an opening that is constantly established in normal running and is of appropriate size to keep the specific gravities of distillate leaving said condensing means within twenty four one thousandths of those obtained in corresponding periods in a test run in which such passing vapors have formed condensate at the rate of two per cent. by volume of an original charge per hour, and (3) controlling said heating and confining the liquid contents of the still in such manner as to maintain the oil is distillation at a decomposing temperature and under a pressure of evolved vapors which is above a minimum within the pressure mentioned, substantially as described.

12. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form to temperatures sufficient to effect decomposition of the oil under a superatmospheric pressure of not less than thirty pounds per square inch, when the still contents are suitably confined, (2) conducting the evolved vapors to condensing means through an opening that is constantly established in normal running and is not alterable automatically by variations of pressure either to be automatically closed and reestablished by such variations or to be otherwise varied

automatically thereby and is of appropriate size to keep the specific gravities of distillate leaving said condensing means within twenty four one thousandths of those obtained in corresponding periods in a test run in which such passing vapors have formed condensate at the rate of two per cent. by volume of an original charge per hour, and (3) controlling said heating and confining the liquid contents of the still in such manner as to maintain the oil in distillation at a decomposing temperature and under a pressure of evolved vapors which is above a minimum within the pressure mentioned, substantially as described.

13. The process of distilling petroleum or other hydrocarbon oil under a superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form to temperatures sufficient to effect decomposition of the oil under a superatmospheric pressure of not less than thirty pounds per square inch, when the still contents are suitably confined, (2) conducting the evolved vapors to condensing means through an opening that is constantly established in normal running and can be closed and reestablished and also varied in size manually by an attendant and that is of appropriate size to keep the specific gravities of distillate leaving said condensing means within twenty four one thousandths of those obtained in corresponding periods in a test run in which such passing vapors have formed condensate at the rate of two per cent. by volume of an original charge per hour, and (3) controlling said heating and confining the liquid contents of the still in such manner as to maintain the oil in distillation at a decomposing temperature and under a pressure of evolved vapors which is above a minimum within the pressure mentioned, substantially as described.

14. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch, sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures that are below

the respective points at which the ordinary vapor tension of the undecomposed oil is estimated to equal the still pressure, to wit, when the still pressure is thirty pounds superatmospheric effecting said decomposition at temperatures not so much as seventy three degrees F. above those attained in a parallel distillation under atmospheric pressure, when the still pressure is seventy five pounds superatmospheric effecting said decomposition at temperatures not so much as one hundred and thirty one degrees F. above the so attained temperatures, and when another still pressure is employed effecting said decomposition at temperatures within a corresponding maximum above the so attained temperatures, (3) cooling the evolved vapors to between one hundred and fifty and three hundred and fifty degrees F. below the contemporaneous temperatures of the oil in distillation, (4) returning the so formed condensate to the oil in distillation, and (5) condensing the residue of said vapors as distillate, substantially as described.

15. The process of distilling petroleum or other hydro- [fol. 1205] carbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch, sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures that are below the respective points at which the ordinary vapor tension of the undecomposed oil is estimated to equal the still pressure, to wit, when the still pressure is thirty pounds superatmospheric effecting said decomposition at temperatures not so much as seventy three degrees F. above those attained in a parallel distillation under atmospheric pressure, when the still pressure is seventy five pounds superatmospheric effecting said decomposition at temperatures not so much as one hundred and thirty one degrees F. above the so attained temperatures, and when another still pressure is employed effecting said decomposition at temperatures within a corresponding maximum above the so attained temperatures, (3) cooling the evolved vapors to below 550° F. and not so low as to prevent the passage over of hydrocarbons, with boiling points intermediate 338° F. to 518° F., (4) returning the so formed

condensate to the oil in distillation, and (5) condensing the residue of said vapors as distillate, substantially as described.

16. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds and not so much as one hundred pounds per square inch sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures that are below the respective points at which the ordinary vapor tension of the undecomposed oil is estimated to equal the still pressure, to wit, when the still pressure is thirty pounds superatmospheric effecting said decomposition at temperatures not so much as seventy three degrees F. above those attained in a parallel distillation under atmospheric pressure, when the still pressure is seventy five pounds superatmospheric effecting said decomposition at temperatures not so much as one hundred and thirty one degrees F. above the so attained temperatures, and when another still pressure is employed effecting said decomposition at temperatures within a corresponding maximum above the so attained temperatures, (3) cooling the so evolved vapors to between one hundred and fifty and three hundred and fifty degrees F. below the contemporaneous temperatures of the oil in distillation, (4) returning so formed condensate to the oil in distillation, and (5) condensing the residue of said vapors as distillate, substantially as described.

17. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds and not so much as one hundred pounds per square inch, sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures that are below the respective points at which the ordinary vapor tension of the undecomposed oil is estimated to equal the still pressure, to wit,

when the still pressure is thirty pounds superatmospheric effecting said decomposition at temperatures not so much as seventy three degrees F. above those attained in a parallel distillation under atmospheric pressure, when the still pressure is seventy five pounds superatmospheric effecting said decomposition at temperatures not so much as one hundred and thirty one degrees F. above the so attained temperatures, and when another still pressure is employed effecting said decomposition at temperatures within a corresponding maximum above the so attained temperatures, (3) cooling the so evolved vapors to below 550° F. and not so low as to prevent the passage over of hydrocarbons with boiling points intermediate 338° F. and 518° F., (4) returning so formed condensate to the oil in distillation, and (5) condensing the residue of said vapors as distillate, substantially as described.

18. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating to decomposing temperatures a batch of said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch, (2) so cooling the evolved vapors in the space above the oil in distillation by exposure of the still top to the atmosphere as to effect a partial condensation of the vapors in said space, (3) protecting said vapors against excessive cooling due to enlargement of said space by diminution in volume of the oil in distillation as well as against superheating above the contemporaneous temperatures of said oil, (4) returning condensate formed by said cooling to the oil in distillation, and (5) conducting residual vapors away for condensation as distillate, substantially as described.

19. The process of distilling petroleum or other hydro- [fol. 1206] carbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating to decomposing temperatures a batch of said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch, (2) so cooling the evolved vapors in the space above the oil in distillation by exposure of the still

top to the atmosphere as to effect a partial condensation of the vapors in said space, (3) protecting said vapors against excessive cooling due to enlargement of said space by diminution in volume of the oil in distillation as well as against superheating above the contemporaneous temperatures of said oil, (4) returning condensate formed by said cooling to the oil in distillation, and (5) conducting residual vapors away through a throttling device for condensation under reduced pressure as distillate, substantially as described.

20. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures under an at least approximately uniform pressure, (3) preserving the evolved vapors from heating above the contemporaneous temperatures of the oil in distillation, (4) allowing the vapors to escape continuously through a throttling device at a sufficiently small rate to produce distillate whose specific gravity will not be more than twenty four one-thousandths (0.024), if any, greater than that of the distillate which would be obtained in a parallel distillation performed at a two per cent per hour rate, and (5) condensing the so escaping vapors as distillate, substantially as described.

21. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate from under a superatmospheric pressure of not less than thirty pounds per square inch sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures under an at least approximately uniform pressure, (3) cooling the evolved vapors under superatmospheric pressure to below 550° F. and not so low as to prevent the passage over of hydrocarbons with boiling points intermediate 338° F. to 518° F., (4) returning the so formed condensate to

the oil in distillation, (5) allowing the uncondensed vapors to escape continuously through a throttling device at a sufficiently small rate to produce distillate whose specific gravity will not be more than twenty four one-thousandths (0.024), if any, greater than that of the distillate which would be obtained in a parallel distillation performed at a two per cent. per hour rate, and (6) condensing the so escaping vapors as distillate, substantially as described.

22. The process of distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which process consists in (1) heating said petroleum or other oil in an appropriate form under a superatmospheric pressure of not less than thirty pounds per square inch sufficiently to induce decomposition of component hydrocarbons, (2) effecting said decomposition at gradually increasing temperatures under an at least approximately uniform pressure, (3) preserving the evolved vapors from heating above the contemporaneous temperatures of the oil in distillation, (4) cooling the evolved vapors under superatmospheric pressure to below 550° F. and not so low as to prevent the passage over of hydrocarbons with boiling points intermediate 338° F. to 518° F., (5) returning the so formed condensate to the oil in distillation, (6) allowing the uncondensed vapors to escape continuously through a throttling device at a sufficiently small rate to produce distillate whose specific gravity will not be more than twenty four one-thousandths (0.024), if any, greater than that of the distillate which would be obtained in a parallel distillation performed at a two per cent. per hour rate, and (7) condensing the so escaping vapors as distillate, substantially as described.

23. Apparatus for distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which apparatus comprises (1) a horizontal cylinder still having its upper part exposed to the atmosphere for cooling and its lower part to fire gases for heating, and an intermediate portion, equal in cubic contents to not less than half the capacity of the still, that is protected both from the atmosphere and from the fire gases, said still being of practical size, strong enough to resist all internal superatmospheric pressure of more than

thirty pounds to the square inch, adapted for batch running in which the volume of oil in the still diminishes during the run, and so constructed interiorly that condensate formed in the vapor space is returned to the oil in distillation, (2) an outside condenser provided with a distillate draw off, (3) a vapor pipe leading from said still to said outside condenser, and (4) means for maintaining a [fol. 1207] superatmospheric pressure in excess of thirty pounds per square inch in said still during distillation, substantially as described.

24. Apparatus for distilling petroleum or other hydrocarbon oil under superatmospheric pressure for obtaining products by decomposition, which apparatus comprises (1) a horizontal cylinder still having its upper part exposed to the atmosphere for cooling and its lower part to fire gases for heating, and an intermediate portion, equal in cubic contents to not less than half the capacity of the still, that is protected both from the atmosphere and from the fire gases, said still being of practical size, strong enough to resist an internal superatmospheric pressure of more than thirty pounds to the square inch, adapted for batch running in which the volume of oil in the still diminishes during the run, and so constructed interiorly that condensate formed in the vapor space is returned to the oil in distillation, (2) an outside condenser provided with a distillate draw off, (3) a vapor pipe leading from said still to said outside condenser, and (4) a vapor throttling device located intermediate said still and said outside condenser and adapted to hold the vapors in said still under superatmospheric pressure in excess of thirty pounds per square inch, while allowing said vapors to escape through said throttling device to said outside condenser, substantially as described.

25. The process of obtaining hydrocarbon products by decomposition of hydrocarbons which process consists in distilling crude petroleum to beyond the point at which the stream at the condenser outlet exhibits a viscosity of one hundred and seventy seconds at 100° F., collecting in this distillation a cut of distillate, free from still wax and like heavy matters of sticky character, which cut begins so far below and ends so far above the point just mentioned that

neither the hydrocarbons therein with viscosities intermediate seventy seconds and one hundred and seventy seconds at 100° F. nor the more viscous hydrocarbons constitute less than 10 per cent. by volume of all the component hydrocarbons thereof with viscosities above seventy seconds at 100° F., and subjecting so obtained and so constituted distillate to distillation at decomposing temperatures, under a superatmospheric pressure of not less than thirty pounds per square inch, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

Morace P. Chamberlain.

Witnesses: G. W. Armstrong, E. A. Cotten.

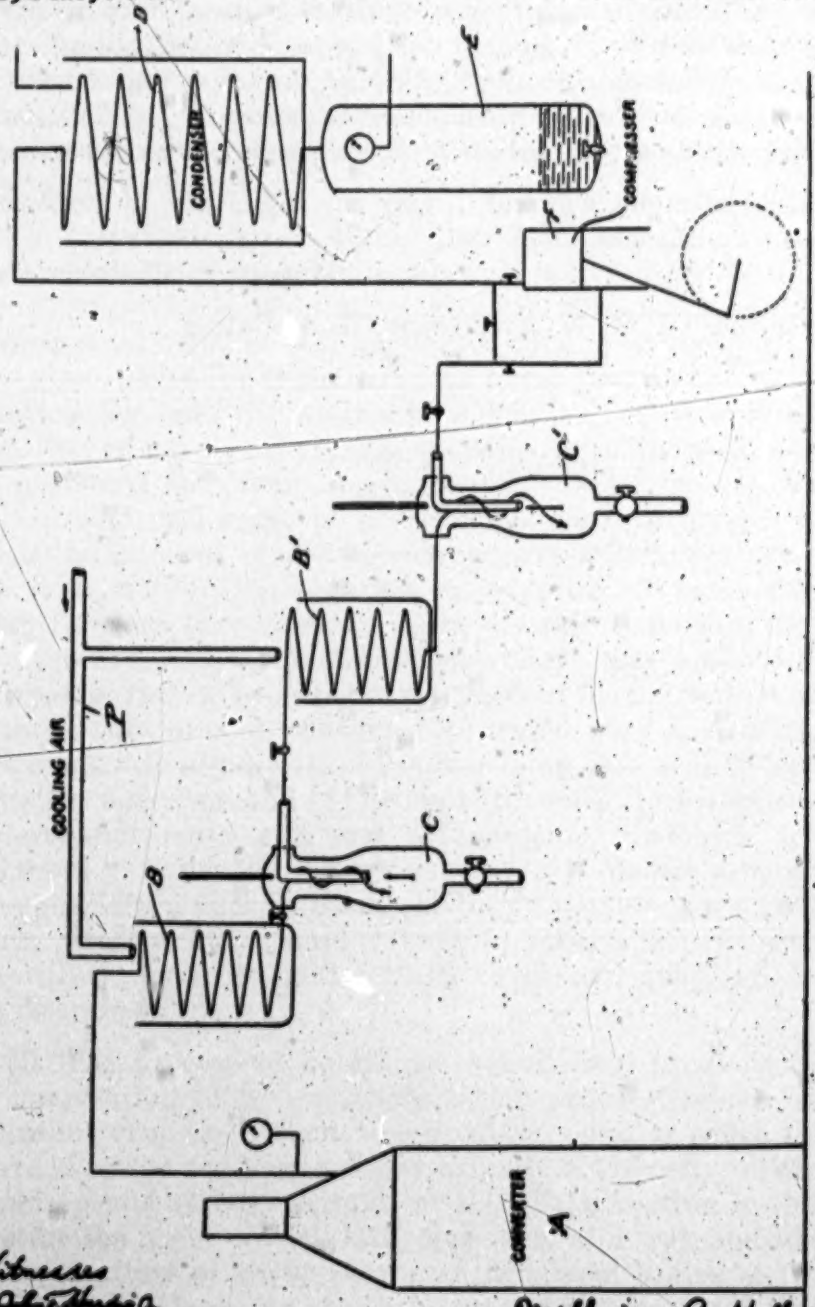
[fol. 1208] PETITIONER'S EXHIBIT 183

W. A. HALL.

PROCESS FOR THE PRODUCTION OF MOTOR SPIRIT FROM HEAVY HYDROCARBONS.

APPLICATION FILED MAR. 12, 1914.

1,242,795. Patented Oct. 9, 1917.



Witnesses
John T. Hodge Jr.
H. McConnell

William A. Hall
by A. B. Fritz Jr. Atty.

[fol. 1209] United States Patent Office

William Augustus Hall, of New York, N. Y.

Process for the Production of Motor-Spirit from Heavy Hydrocarbons

1,242,795. Specification of Letters Patent. Patented Oct. 9, 1917

Application filed March 12, 1914. Serial No. 824,194

To all whom it may concern:

Be it known that I, William Augustus Hall, a citizen of the United States of America, and residing at New York City, New York, United States of America, have invented a certain new and useful Improvement in Processes for the Production of Motor-Spirit from Heavy Hydrocarbons, of which the following is a specification.

This invention relates to an improved process for the production of a liquid motor fuel suitable for use in the usual carburetors of internal combustion engines, from heavier and less volatile hydrocarbons.

The said improved process contemplates the chemical affixation of a hydrocarbon gas to vaporized, normally liquid, chemically unsaturated hydrocarbon, the said gas and liquid having the properties hereinafter specified; there being produced a fourfold effect:

First, a greatly increased volume of fuel produced, over the volume obtained by any of the processes depending entirely upon cracking, with which I am familiar;

Second, a materially lower boiling point than that of said unsaturated hydrocarbon, or of ordinary gasolene obtained by cracking heavier oils;

Third, a lower specific gravity than that of said unsaturated hydrocarbon, or of ordinary gasolene obtained by cracking heavier oils, and

Fourth, greatly increased fractions volatile at comparatively low temperatures, as compared with said unsaturated hydrocarbon, or with ordinary gasolene.

The process forming the subject matter of my present application is not a process of hydrogenation, in the ordi-

nary meaning of that term, for very little free hydrogen is present (either from the cracking or from any other source) and, as far as I have been able to ascertain, none is utilized in any part of the process, and no nickel or other metallic catalyst is present in any part of the apparatus.

My present process is, on the contrary, a process of producing gases containing considerable amounts of condensable hydrocarbons, such as propane, butane, pentane, and hexane and the subsequent affixation of these gases to the vapors of an unsaturated hydrocarbon herein referred to as "liquid base."

In order to produce satisfactory results in accordance with the present process, it is necessary that the "liquid base" and the gases should both be of the proper character. The "liquid base" should best contain considerable quantities of unsaturated hydrocarbons, in order to make the chemical affixation of the gases take place readily. Under certain conditions, however, it appears that some of the gases are chemically affixed to saturated, as well as to unsaturated bodies. The gas must contain considerable amount of hydrocarbons containing at least two or three carbon atoms and can not consist entirely, or even principally of hydrogen and methane, if good results are to be secured. It is preferable that the gases also contain some unsaturated hydrocarbons.

The preferable "liquid base" is that volatile liquid of which the vapors exist (mixed with gases) in the vaporous product produced by cracking a relatively heavy hydrocarbon oil under a pressure of (*e. g.*) about 70 pounds per square inch and at about 600° or 650° C. This temperature is measured by a pyrometer placed between the vertical pipe coils in the furnace A. Thereafter I cool the gases and vapors to a temperature of about 200° C., with or without more or less lowering of pressure. Such a "liquid base" can be produced in other ways, and it is particularly characterized in that it consists essentially of normally liquid hydrocarbons, whose vapors, if cooled under a pressure of about 70 pounds per square inch, with a wet gas (having the composition above referred to), will unite chemically with constituents of said gas, to produce a motor fuel. The said vaporized "liquid base" and gas must be

present together at a temperature materially above atmospheric, for example 100 to 200° C., and under pressure, to produce this union.

The motor fuel does not appear to consist of the "liquid base" with the gases dissolved therein, since the product can be distilled without the loss of more than small amounts of the gaseous portions which have been affixed to the "liquid base." If the product were solely a solution of the gases in the "liquid base", the gases would be lost if the product were distilled. Of this "liquid base", the more volatile portions, especially, usually contain large amounts (say 30 to 50%) of hydrocarbons of the ethlene series, unsaturated hydrocarbons.

This "liquid base", in the preferred mode of execution [fol. 1210] of the process, is made by cracking a cheap hydrocarbon, for instance, a distillate such as gas oil. A suitable gas oil is one having a specific gravity of from about 34 to about 40° Bé. and an initial boiling point of from about 80 to about 180° C.

A construction of apparatus suitable for the performance of the improved process is illustrated diagrammatically in the figure of the accompanying drawing.

Referring to the drawing, A denotes a converter in which the gas oil is subjected to a temperature of about 650° C., under a pressure of about 70 pounds per square inch, whereby the oil is cracked and a considerable portion gasified. From the converter A the mixture of oil vapor and gas is passed through suitable coolers B, B′ (cooled by a suitable fluid introduced through pipes P) whereby the temperature of the mixture is lowered to about 200° C. C, C′ denote separators in which the major part of all fractions non-volatile at about 200° C. is removed, in the liquid state, from the remaining gases and vapors. The vapors of liquid, which are volatile at a temperature of approximately 200° C., together with any mist of condensed liquid particles which may be carried along, together with the gases present, may then be conducted directly through a cooler or condenser D, under approximately the pressure of the converter, and the condensate collected in the receptacle, E or may be still further compressed by means of a mechanical compressor indicated conventionally at F. The liquid, the vapor of which passes with the gas to

the compressor is that herein referred to as the "liquid base".

Such a liquid is itself not a satisfactory fuel for motor cars. It is this liquid which unites with the gases, during the compression and subsequent cooling, to produce the motor fuel.

In some respects this "liquid base" is similar to the well known cracked hydrocarbon spirits at present produced by cracking oils of higher boiling points than ordinary gasolene, such as crude oil or solar oil which have little or no value as a motor car fuel unless redistilled and cut at a low temperature, *e.g.* about 150° C., at which point the yield is very small.

In a converter, I produce the vapors of such a "liquid base", but in the final condensation I obtain a product having a low boiling point, and a large fraction volatile at low temperatures, the product being different from the "liquid base", on account of the affixation of gases thereto.

The "liquid base" may, for example be made by heating to a temperature of above 500° C., an oil known as "Crown Diamond paraffin oil", a low grade burning oil of about .815 specific gravity. The "liquid base" so produced is a product having a gravity of about .769 (at 15° C.), and which has the following distillation table:

First drop	31° C.
Total distillate up to 50° C	1%
" " " " 60	2%
" " " " 80	6%
" " " " 100	14%
" " " " 150	50%
" " " " 160	57%

Such a "liquid base" or half product is found to be an excellent medium, to which to affix the wet gas. The product produced by compressing the vapors of this "liquid base", with the gases present was a product with a gravity of .755 (at 15° C.) with the following distillation table:

First drop	30° C.
Total distillate up to 50° C	2 %
" " " " 60	5 %
" " " " 80	15 %
" " " " 100	23 %
" " " " 150	48.5%
" " " " 160	60 %

The invention is, of course, not limited to this specific example, which is given merely for the purpose of showing the difference between the "liquid base" and the "motor fuel." On account of the chemical affixation produced, I am to cut the spirit at a high temperature, say 200° C., or even high, (as compared with 150, in the case of "cracked gasolene"), thereby obtaining a much greater yield and more calorific value.

If desired I may so conduct the operation in the converter as to produce the desired qualities and quantities of gas and "liquid base," which with some oils such as gas oil and heavy distillates above the lubricant fractions can be obtained by the cracking of said oils at about 650° C. under 70 to 80 pounds pressure, while maintaining the proper speed of flow. In this way there is produced a large amount of gas, which if separated, would remain as a permanent gas at ordinary atmospheric conditions, but a large portion of which gas will combine chemically with the spirit portion of the "liquid base" after the tarry and heavy residues have been removed, provided the gases and the "liquid base" (while the latter is in a state of vapor) be subjected to sufficient pressure, while at a temperature of from 100° C. to 200° C.

Certain oils do not readily respond to the cracking process and from such oils a sufficient amount of the desired "liquid base" cannot be obtained to supply the medium for the affixation of the gas produced. Yet such oils may produce with ease large quantities of the gas desired. In such cases it may be found desirable to produce the gas or the largest portion of it from one oil, and the "liquid [fol. 1211] base" from another oil, and to combine them in the manner herein set forth.

I am aware that heavy hydrocarbon liquids have been charged with hydrocarbon gases, as is done in the production of the so-called "natural gas gasolene" or "casing-head gasolene," but such processes, as far as I am aware, are based in most cases on the principle of solution and accomplished by high pressure and refrigeration, it being known that most gases are far more soluble in cold solvents than in hot. I believe, however, that it has not heretofore been proposed to affix such gases chemically to a "liquid base" while the latter was at a high temperature and in a state of vapor, the "liquid base" being a spirit obtained

by cracking and containing a large proportion of ethylene hydrocarbons which "liquid base" is effective for the chemical affixation of hydrocarbon gases.

It is to be noted that in carrying out the process of the present application, I preferably do not add water, hydrogen or gases containing hydrogen, or carbon monozid to the oil or oil vapors. Also I do not treat the gases and vapors with any catalytic material.

While I have stated that the pressure in the coils B, B', C, and C' may be much lower than in the converter A, this feature is not claimed herein, but in my copending application No. 829,634, filed April 4, 1914.

I claim:

1. A process of making a motor fuel which comprises producing a mixture of vapors and gases, said vapors containing a considerable percentage of compounds of the ethylene series, by cracking hydrocarbon oil under a pressure materially above atmospheric and at a temperature not lower than about 500° C., separating out those portions of the vapors having boiling points of about 200° C. and above, leaving a mixture of gases and vapors at a temperature of over 100° C., and thereafter cooling said mixture including the gases and remaining vapors while under a pressure materially above atmospheric, to condense out a motor fuel.

2. A process of making a motor fuel which comprises heating portions of different hydrocarbon oils, to temperatures in excess of 600° C., under a pressure materially above atmospheric, cooling the gases and vapors thereby produced, down to at least about 200° C. but down to 100° C., to condense products having high boiling points, and removing at least the major part of the condensate from the remaining gases and vapors, subjecting the remaining gases and vapors thereby produced while still in a heated condition, to pressure materially above atmospheric, and finally further cooling the gases and vapors while under a pressure materially above atmospheric to condense out the motor fuel.

3. A process of producing a motor fuel, which comprises cracking a hydrocarbon oil under pressure materially above atmospheric, at a temperature sufficiently high to convert a portion of the oil into fixed gases, and to produce vapors

containing considerable percentages of unsaturated hydrocarbons; cooling the vapors and gases sufficiently to cause the portions having boiling points of about 200° C., to condense out; and thereafter subjecting the resulting gases and vapors at a temperature of 100 to 200° C., to a pressure of not less than about 70 pounds per square inch, to produce a chemical affixation of the gases and vapors.

4. A process of making a motor fuel, which comprises cracking a mineral oil under a pressure of several atmospheres, at a temperature of above 500° C., cooling the gases and vapors, while still under a pressure of several atmospheres, to a temperature of not over about 200° C., to separate out materials having high boiling points, thereby producing a mixture containing the gases and containing the vapors of those portions which remain in vapor form at the temperature employed in said step, subjecting said mixture to a pressure above that used in the said cooling step, and thereafter cooling said mixture while under a pressure at least as great as that employed in the cracking operation, to condense out the motor fuel.

5. A process of making a motor fuel from hydrocarbons of higher boiling points, which comprises cracking said hydrocarbons by passing the same through a chamber at a temperature of about 600° C., under a pressure of several atmospheres, separating from the gases and vapors thereby produced, a part at least of the constituents thereof which have boiling points above 200° C., thereby producing a mixture of gases and non-condensed vapors at a temperature of 100 to 200° C., subjecting said mixture to a pressure materially above atmospheric, and thereafter cooling said mixture under a pressure not less than used in the first step, to condense out the motor fuel.

6. A process of making a motor fuel which comprises cracking hydrocarbon oils at 600 to 650° C., under a pressure of about 70 pounds per square inch, thereafter cooling the resulting gases and vapors to about 200° C., to separate the most readily condensable portions therefrom, subjecting the remaining gases and vapors to a pressure of at least about 70 pounds per square inch, and cooling the same while under a pressure of several atmospheres, to condense out the motor fuel.

[fol. 1212] 7. A process of making a motor fuel from hydrocarbons of higher boiling points, which comprises cracking said hydrocarbons by passing the same through a chamber at a temperature of at least 600° C., under a pressure materially above atmospheric, separating from the gases and vapors thereby produced, while still under a pressure materially above atmospheric, a part at least of the constituents thereof having boiling points above 200° C., then cooling the remaining gases under a pressure not less than that used in the first step, to condense out the motor fuel.

8. In the manufacture of motor fuel, the improvement which comprises subjecting to a pressure of about four atmospheres, a mixture including hydrocarbon gases and also including those portions of the vapors of a cracked hydrocarbon liquid which are volatile at about 200° C., without material amounts of hydrocarbons having boiling points much above 200° C., and thereafter cooling the remaining mixture of gases and vapors while under a pressure of several atmospheres substantially as described.

9. In the manufacture of motor fuel, the herein described improvement which comprises chemically affixing hydrocarbon gases to a vaporizing "liquid base," composed of hydrocarbons liquid at ordinary temperature, the larger part of which are volatile at a temperature of about 200° C., by subjecting a mixture of said materials to a pressure materially above atmospheric, while at a temperature not materially below 100° C., and thereafter cooling the resulting mixture under a pressure materially above atmospheric to condense the motor fuel.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

William Augustus Hall.

Witnesses: H. D. Jameson, G. C. Francis.

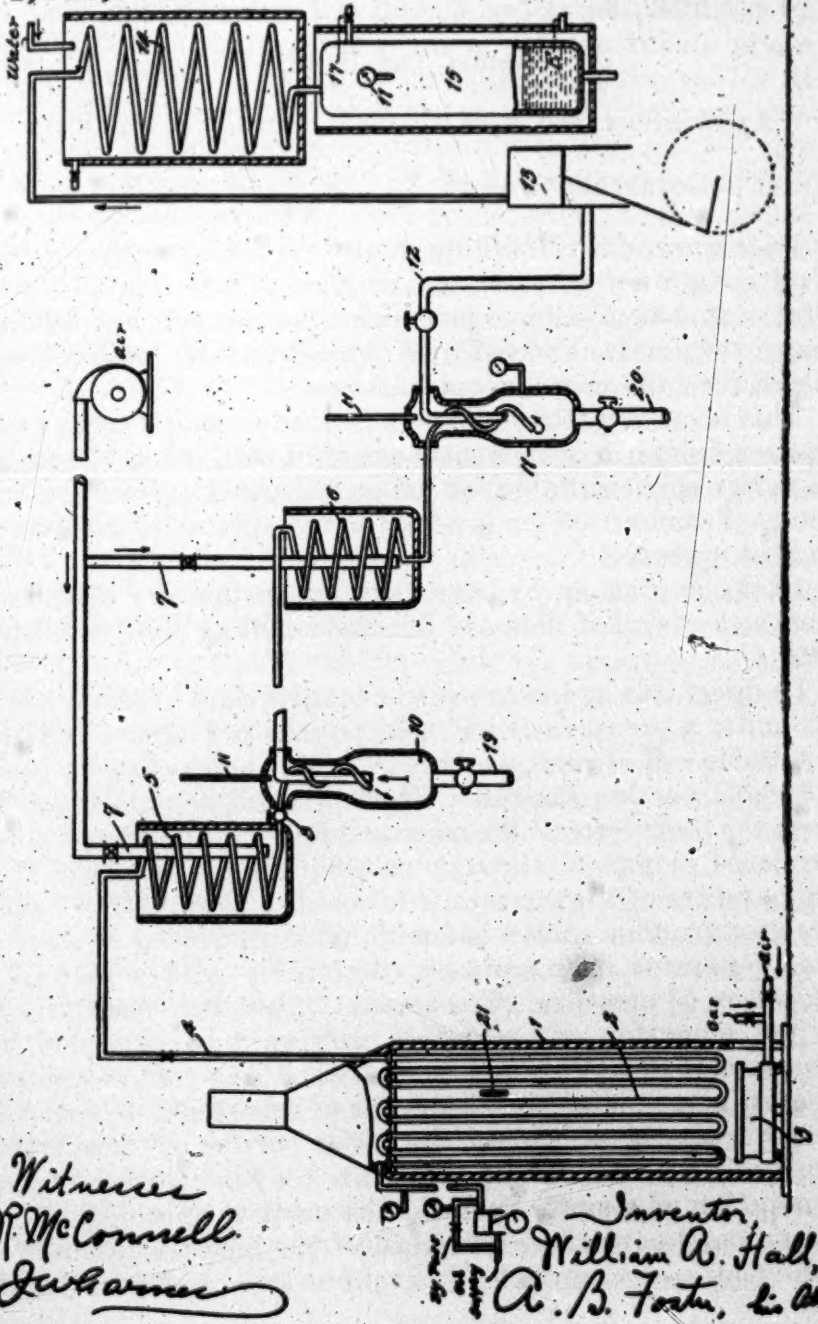
[fol. 1213] PETITIONER'S EXHIBIT 184

W. A. HALL.

PRODUCING MOTOR FUEL.

APPLICATION FILED APR. 4 1914.

1,242,796. Patented Oct. 9, 1917.



Witnesses
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Inventor,
William A. Hall, by
A. B. Foster, his Atty.

[fol. 1214] United States Patent Office

William Augustus Hall, of New York, N. Y.

Producing Motor-Fuel

1,242,796. Specification of Letters Patent.

Patented Oct. 9, 1917

Application filed April 4, 1914. Serial No. 829,634

To all whom it may concern:

Be it known that I, William Augustus Hall, a citizen of the United States of America, and resident of New York, United States of America, have invented a certain new and useful Improvement in Processes of Producing Motor-Fuel, of which the following is a specification.

This invention relates to an improved process for the production from heavy hydrocarbons of liquid fuels in the form of motor spirit suitable for use in the usual carburetors of internal combustion engines and to the apparatus employed in said process.

I take any cheap hydrocarbon, for instance, a distillate such as a gas oil of 40 to 44° Bé., and a boiling point of about 110° C.

I subject this hydrocarbon to a temperature of about 650° C., under a pressure of about 70 pounds per square inch in a suitable coil of pipe, whereby the oil is cracked and a considerable portion gasified. From this coil of pipe which I term the "converter" the mixture of oil vapor and gas thus produced is passed through suitable coolers whereby the temperature of the mixture is lowered to about 200° C. and the mixture thus cooled is fractionally condensed in a suitable separator or separators, preferably with a material reduction of pressure. The amount of pressure maintained in the separator or separators may vary considerably, a pressure of 20 to 25 pounds per square inch (above atmospheric) being suitable. The object of this step is to remove from the gases and vapors, the major portion of those fractions, of which the boiling points are too high for use in the production of a motor fuel, for the purpose specified. The major portion of those fractions of the mixture which are non-volatile at about 200° C., are thus separated in a liquid

state, from the remaining gases and vapors, which gases and vapors, are then recompressed, at a temperature of approximately 200° C., to a pressure of about 70 pounds per square inch, by means of any suitable mechanical compressor, and then condensed under pressure in the cooler.

I have found that if the gases and vapors produced by cracking heavy hydrocarbons under the conditions above indicated and from which those fractions condensable at about 200° C. have here been separated by fractional condensation, are maintained in contact with one another at a temperature say about 200° C., and under a pressure of about 70 pounds per square inch or more and are then cooled together not only are the vapors of the liquid hydrocarbons condensed but that a considerable quantity of the easily liquefiable gaseous hydrocarbons are also condensed and that from the final condensed liquid these condensed gases (whatever may be the reason whether chemical or otherwise) do not escape at ordinary temperatures.

Apparatus suitable for the performance of the improved process is illustrated diagrammatically in the figure of the accompanying drawing.

Referring to said drawings, 1 denotes a cracking apparatus or converter, containing a coil of pipe 2, in which the hydrocarbon oil is subjected to a temperature of about 650° C., and under a pressure of 70 pounds per square inch, more or less. This temperature is measured by a pyrometer 21, placed between the coils of pipe, 2 as shown.

The heat is supplied by means of a burner 3, by which operation the oil is cracked and a considerable proportion thereof is gasified. From this converter a connection 4 leads to cooling coils 5 and 6, which may be cooled by air or by other suitable cooling fluid blown in through the tubes 7 and serving as coolers whereby the temperature of the mixture of oil vapor and gas is lowered to about 200° C. The mixture of gases and vapors, thus cooled, and also preferably reduced in pressure, and by suitably disposed valves, including the valve 8, in the piping, is then fractionally condensed and separated in suitable separators 10 and 11, whereby those portions of the mixture, liquid at about 200° C. are extracted from the vapors and gases, in the form of a liquid. This liquid may be drawn off through the pipes 19 and 20, provided with suitable valves and with suitable cooling means as illustrated. The gas and vapors pass by

pipes 12 to a compressor 13 and are then forced through the pipe 14, which is surrounded by a cooling fluid, such as water, thence into the receptable 15, which is likewise water-jacketed, and in the parts 14 and 15, a pressure for example [fol. 1215] 70 pounds per square inch is maintained by means of the compressor 13. Upon the amount of pressure employed in this step, will depend, to a certain extent, the properties of the product.

In the preferred form of execution of the process, I lower the pressure considerably, so that during the first cooling operation, in the coolers 5 and 6, and in the traps 10 and 11, a pressure materially below that employed in the cracking operation prevails, that is to say, the cracking operation is effected at a pressure of, say about 70 lbs. per square inch. The pressure is then released and the gases and vapors cooled to about 200° C., (or say to about 160 or 200° C.), while at a low pressure, which may be atmospheric or slightly more, under which conditions the solid carbon, tarry matters, any uncracked oil present, and substantially all products not volatile at the temperature of the cooling are condensed and separated, after which the pressure is again raised to 70 lbs. per square inch, or more, before the final cooling and condensation.

This drop in pressure in the preliminary condensation is of especial value in the process, and constitutes a material improvement over the modification of the process in which the pressure is held up to (or near) the pressure of the cracking coil. By this lowering of pressure, the operation of removing the tarry matters and especially the solid matter (free carbon, etc.) is greatly accelerated, and moreover the entire apparatus is very much simplified, and the maintenance of a uniform temperature at the outlet of the trap 11, and a uniform composition of this material, is made much easier.

By thus lowering the pressure and cooling to the desired temperature, substantially all of the free carbon and very difficultly volatile material separates in the first trap 10, and the material which separates in the second cooler and trap is free from solid carbon and free from coke-like material, and this second condensate (termed "light residue") can be directly employed for making a second "run" through the apparatus, without filtration or other preliminary treatment.

Another reason why I prefer to lower the pressure during the preliminary condensation is the following: It is well known that the boiling point of a given liquid (and likewise the temperature at which the vapor of such liquid condenses to the liquid state) is dependent upon the existing pressure. Lowering the pressure lowers the boiling point.

Moreover, by lowering the pressure during the condensation operation, it is possible to secure a much more accurate condensation, while removing the undesirable fractions, and while leaving in some of the desirable constituents which would be removed if the preliminary condensation were effected at or near the converter pressure.

A pipe 17 serves to lead from the upper end of the condenser the non-condensable portion of the gases.

The cracking of oil under pressure by heat lower than indicated and the separation during distillation of the heavier fractions by fractional condensation are not in themselves new but it is the combination of these processes so carried out as to produce both vapors and gases together with the subsequent condensation under pressure of the mixed vapors of liquid hydrocarbons and the easily liquefiable gaseous hydrocarbons which constitutes the essence of my invention.

The modification of the process in which the pressure of the gases and vapors is not lowered in the preliminary cooling step (separation of tarry matters) is included in the claims of my copending application Serial No. 824,194, filed Mar. 12, 1914.

What I claim is:

1. A process of making a motor fuel which comprises cracking hydrocarbon oils at a temperature of about 600 to 650° C., under a pressure of about 70 pounds per square inch, thereafter cooling the resulting gases and vapors to about 200° C., while said gases and vapors are at a lower pressure to separate the most readily condensable portions therefrom, increasing the pressure of the remaining gases and vapors, to a pressure of at least about 70 pounds per square inch, and thereafter cooling the mixture of gases and vapors to condense the product.

2. A process of making a motor fuel from an oil of high boiling points, which comprises cracking said oil under a

pressure exceeding four atmospheres, at a temperature of not less than about 600° C., thereby producing a mixture comprising gases and vapors of both high and low boiling points, thereafter lowering both the temperature and pressure sufficiently to remove the fractions of higher boiling points, thereafter increasing the pressure to over four atmospheres and then further lowering the temperature sufficiently to condense the product.

3. A process of producing a motor fuel from oil distillates having boiling points higher than gasolene, said process comprising, first, cracking said oil, under a pressure of about 70 pounds per square inch, and at a temperature materially above 500° C., second, lowering the temperature of the gases and vapors to about 200° C., while allowing the pressure to drop somewhat; third, compressing the gases and vapors to a pressure of at least 70 pounds per square inch, and fourth, cooling the same under said pressure, to condense the motor fuel.

[fol. 1216] 4. A process of producing a motor fuel which comprises cracking a hydrocarbon oil under a pressure materially above atmospheric at a temperature sufficient to form gases, and vapors of materials having high boiling points, and unsaturated hydrocarbon vapors, then cooling the gases and vapors, at a pressure materially lower than that used in the cracking operation, to a temperature of above 100° C., but not above about 200° C., to remove materials having higher boiling points, thereafter subjecting the remaining gases and vapors, at a temperature of 100 to 200° C., to a pressure of not less than about 70 pounds per square inch, and thereafter cooling the gases and vapors to condense the motor fuel.

5. A process of producing a motor fuel which comprises cracking a hydrocarbon oil under a pressure materially above atmospheric at a temperature sufficiently high to convert a portion of the oil into fixed gases, and to produce vapors containing considerable percentages of unsaturated hydrocarbons, cooling the vapors and gases, while under a pressure materially below that employed in the cracking operation, sufficiently to separate the portions having boiling points above about 200° C., thereafter subjecting the remaining gases and vapors, at a temperature of 100 to 200° C., to a pressure materially above that used in the said cool-

ing step, and then cooling the gases and vapors sufficiently to cause condensation of the motor fuel.

6. A process of making a motor fuel, which comprises cracking a mineral oil under high pressure, at a temperature above 500° C., cooling the gases and vapors, while at a pressure materially below that used in the cracking operation, to a temperature of not over about 200° C., to separate out materials having high boiling points, further compressing the gases and vapors remaining from said cooling step, and cooling the gases and vapors while in said compressed state, to condense out the motor fuel.

7. A process of making a motor fuel which comprises cracking hydrocarbon oils at a temperature above 500° C., under a pressure of about 70 pounds per square inch, lowering the pressure of the resulting gases and vapors, down to a pressure not greatly exceeding atmospheric, cooling the gases and vapors to a temperature below 200° C., but not materially below 100° C., to separate the most readily condensable portions therefrom, recompressing the gases to a pressure of at least 70 pounds per square inch, and cooling the remaining gases and vapors, under said pressure.

8. A process of producing a motor fuel which comprises passing a current of hydrocarbon oil at a pressure of about 70 pounds per square inch through a pressure-resisting tortuous pipe, located in a furnace heated to approximately 600° C.; reducing the pressure of the gases and vapors, while cooling the same to a temperature of about 200° C., and removing the condensed materials; recompressing the gases and vapors while materially above ordinary atmospheric temperature, to a pressure of approximately 70 pounds per square inch, and thereafter cooling the gases and vapors to condense the motor fuel.

9. A process of producing, from mineral oil, a liquid fuel suitable for use in internal combustion engines, consisting in cracking the oil under a pressure materially above atmospheric to produce gases and vapors, expanding such gases and vapors, and cooling the same to a temperature sufficiently low to condense out material not sufficiently volatile for use as motor fuel, removing such condensed material and thereafter subjecting the remaining gases and vapors, to an increase in pressure, while the gases are in a heated state, and condensing the product so formed.

10. A process of producing a motor fuel which comprises cracking oil under a pressure of several atmospheres at a high temperature to produce gases and vapors, releasing the pressure of the gases and vapors produced within a short time after their production, cooling said gases and vapors to separate such material as is not readily volatile, mechanically compressing the partially cooled, but still warm vapors and gases from which the fractions of high boiling points have been separated, cooling and condensing the products resulting from said compression, while under a pressure of several atmospheres.

11. A process of producing a liquid motor fuel, which comprises cracking an oil at a high temperature under a pressure, materially above atmospheric, to produce gases and vapors, releasing the pressure of the gases and vapors shortly after their production, passing the gases and vapors through a dephlegmator to remove materials of relatively high boiling points from those of relatively low boiling points, mechanically compressing the vapors and gases remaining, and further cooling and condensing the products.

12. A process of producing a motor fuel which comprises (*a*) passing hydrocarbon oil containing fractions having higher boiling points than ordinary gasolene, in the form of a flowing current through a tubular retort under a pressure of approximately 70 pounds per square inch maintained at a temperature of about 650° C., whereby the oil is cracked and a considerable portion is gasified, (*b*) thereafter lowering the pressure to approximately atmospheric, lowering the temperature to approximately 200° C., in order [fol. 1217] to condense and separate at least a portion of the products of high boiling points, (*c*) recompressing the gases and vapors to a pressure of approximately 70 pounds per square inch, while at a temperature of approximately 200° C., and thereafter (*d*) cooling the remaining gases and vapors together, to condense out the motor fuel.

13. A process of making a motor fuel which comprises cracking a flowing current of hydrocarbon oil at a temperature of about 600 to 650° C., under a pressure of about 70 pounds per square inch, thereafter cooling the resulting gases and vapors to about 200° C., while said gases and vapors are at a lower pressure than that used in the cracking operation, to separate at least a portion of the most

readily condensable fractions, increasing the pressure of the remaining gases and vapors, while still at a temperature above normal atmospheric temperature, to a pressure of at least about 70 pounds per square inch, and thereafter cooling the mixture of gases and vapors to condense the product.

14. A process of producing a motor fuel which comprises heating a flowing current of hydrocarbon oil containing fractions having higher boiling points than ordinary gasolene, under pressure materially above atmospheric, to a temperature capable of cracking the said oil with the production of permanent gases, lowering both the pressure and temperature of the gases and vapors thereby produced, sufficiently to separate out fractions having boiling points too high for use in the production of a gasolene substitute, recompressing the remaining mixture of gases and vapors, while at a temperature materially above atmospheric, and thereafter cooling the remaining gases and vapors under superatmospheric pressure, to condense out the motor fuel.

15. A process of making a motor fuel from an oil of high boiling points which comprises cracking a flowing current of said oil under a pressure exceeding four atmospheres, at a temperature of not less than about 600° C., thereby producing a mixture comprising gases and vapors of both high and low boiling points, thereafter lowering both the temperature and pressure sufficiently to remove at least a portion of the fractions of high boiling points, thereafter increasing the pressure in the remaining gases and vapors, while the temperature of the same is above normal atmospheric temperature, and thereafter further lowering the temperature sufficiently to condense the product.

16. A process of producing a motor fuel which comprises cracking a hydrocarbon oil under pressure materially above atmospheric, at a temperature of about 500 to 650° C., to form permanent gases and vapors of materials having high boiling points, and unsaturated hydrocarbon vapors, thereafter cooling such gases and vapors while at a pressure materially lower than that employed in the cracking operation, to a temperature of not above approximately 200° C., to remove materials having high boiling points, thereafter subjecting the remaining gases and vapors, while at a temperature of 100 to 200° C., to a pressure of not less than about

70 pounds per square inch, and thereafter cooling the gases and vapors to condense the motor fuel.

17. A process of producing a motor fuel suitable for use in carbureters of internal combustion engines, from oil distillates having boiling points higher than ordinary gasolene, said process comprising first cracking said oil under a pressure of about 70 pounds per square inch, in the form of a flowing current, at a temperature materially above 500° C., second lowering the temperature of the gases and vapors to about 200° C., while allowing the pressure to drop somewhat, third recompressing the gases and vapors to a pressure of at least 70 pounds per square inch while said gases and vapors are at a temperature materially above ordinary atmospheric temperature, and fourth, cooling the remaining gases and vapors under said pressure, to condense the motor fuel.

18. A process of producing a motor fuel which comprises cracking a hydrocarbon oil under a pressure materially above atmospheric, at a temperature of about 500 to 600° C., to convert a portion of the oil into fixed gases, and to produce vapors containing considerable percentages of unsaturated hydrocarbons, cooling the vapors and gases, while under a pressure materially below that employed in the cracking operation, sufficiently to separate the portions having boiling points above about 200° C., thereafter subjecting the remaining warm gases and vapors, to a pressure materialy above that used in the said cooling step, and then cooling the gases and vapors sufficiently to cause condensation of the motor fuel.

19. A process of making a motor fuel which comprises cracking hydrocarbon oils at a temperature of 600 to 650° C., under a pressure of about 70 pounds per square inch, lowering the pressure of the resulting gases and vapors, down to a pressure not greatly exceeding atmospheric cooling the gases and vapors to a temperature below 200° C., to separate the most readily condensable portions therefrom, recompressing the gases to a pressure of at least 70 pounds per square inch, and cooling the remaining gases and vapors, under said pressure.

20. A process of producing a motor fuel, which comprises [fol. 1218] cracking a hydrocarbon oil under a pressure ma-

terially above atmospheric to produce gas and vapor, cooling the gas and vapor while at a pressure materially below that used in the cracking operation, sufficiently to separate the materials of high boiling points; thereafter subjecting the resulting gases and vapors while at a temperature above atmospheric, to a pressure materially greater than that used in said first cooling operation, and thereafter further cooling the gases and vapors, under a pressure of several atmospheres.

21. A process of producing a motor fuel, which comprises cracking a hydrocarbon oil under pressure materially above atmospheric, to produce gas and vapor, cooling the gas and vapor while at a pressure materially below that used in the cracking operation, sufficiently to separate the materials of high boiling points; thereafter subjecting the resulting gases and vapors while at a temperature above ordinary atmospheric temperature, to a pressure of not less than 70 pounds per square inch, and thereafter cooling the gases and vapors under a pressure of several atmospheres.

22. A process of making a motor fuel, which comprises cracking a mineral oil under high pressure, at a temperature above 500° C., cooling the gases and vapors, while at a pressure materially below that used in the cracking operation, to a temperature of not over 200° C., to separate out materials having high boiling points, further compressing the gases and vapors remaining from said cooling step while still in a heated condition, and cooling the gases and vapors while in said compressed state, to condense out the motor fuel.

23. A process of producing a motor fuel from hydrocarbon oil consisting in cracking said oil under superatmospheric pressure at a temperature upward of 600° C., thereby forming gases and vapor, reducing the pressure of the gases and vapor and separating by fractional condensation that portion of the liquid which is non-volatile at a temperature of approximately 200° C., recompressing the remaining hot gases and vapors, and condensing them together under pressure to produce a liquid substantially as described.

24. A process of producing a motor fuel which comprises passing a current of hydrocarbon oil at a pressure of about

70 pounds per square inch through a pressure-resisting tortuous pipe, located in a furnace heated to approximately 600° C., reducing the pressure of the gases and vapors, while cooling the same to a temperature of about 200° C., and removing the condensed materials; recompressing the gases and vapors while at said temperature, to a pressure of approximately 70 pounds per square inch and thereafter cooling the gases and vapors to condense the motor fuel.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

William Augustus Hall.

Witnesses: H. D. Jameson, O. J. Worth.

[fol. 1219]. PETITIONER'S EXHIBIT 185

J. H. ADAMS.
OIL CONVERTING APPARATUS.
APPLICATION FILED DEC. 1, 1909.

1,320,354. Patented Oct. 28, 1919.

7 SHEETS—SHEET 1.

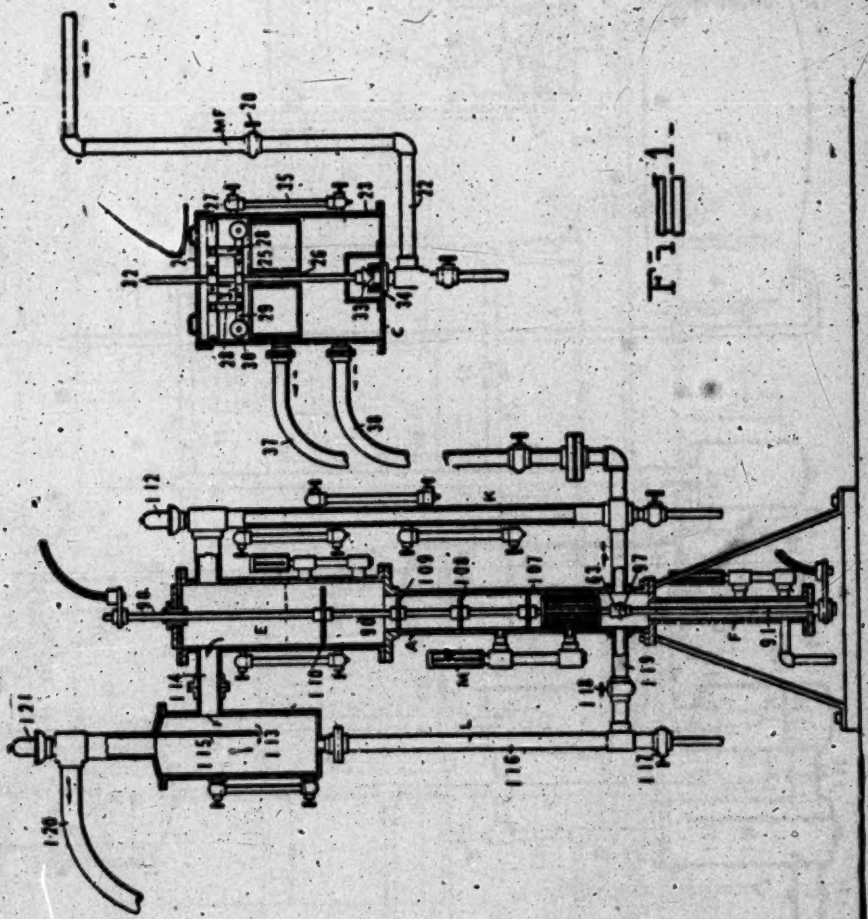

FIG. 1.

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4564

[fol. 1220]

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OIL CONVERTING APPARATUS.

APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

4 SHEETS—SHEET 2.

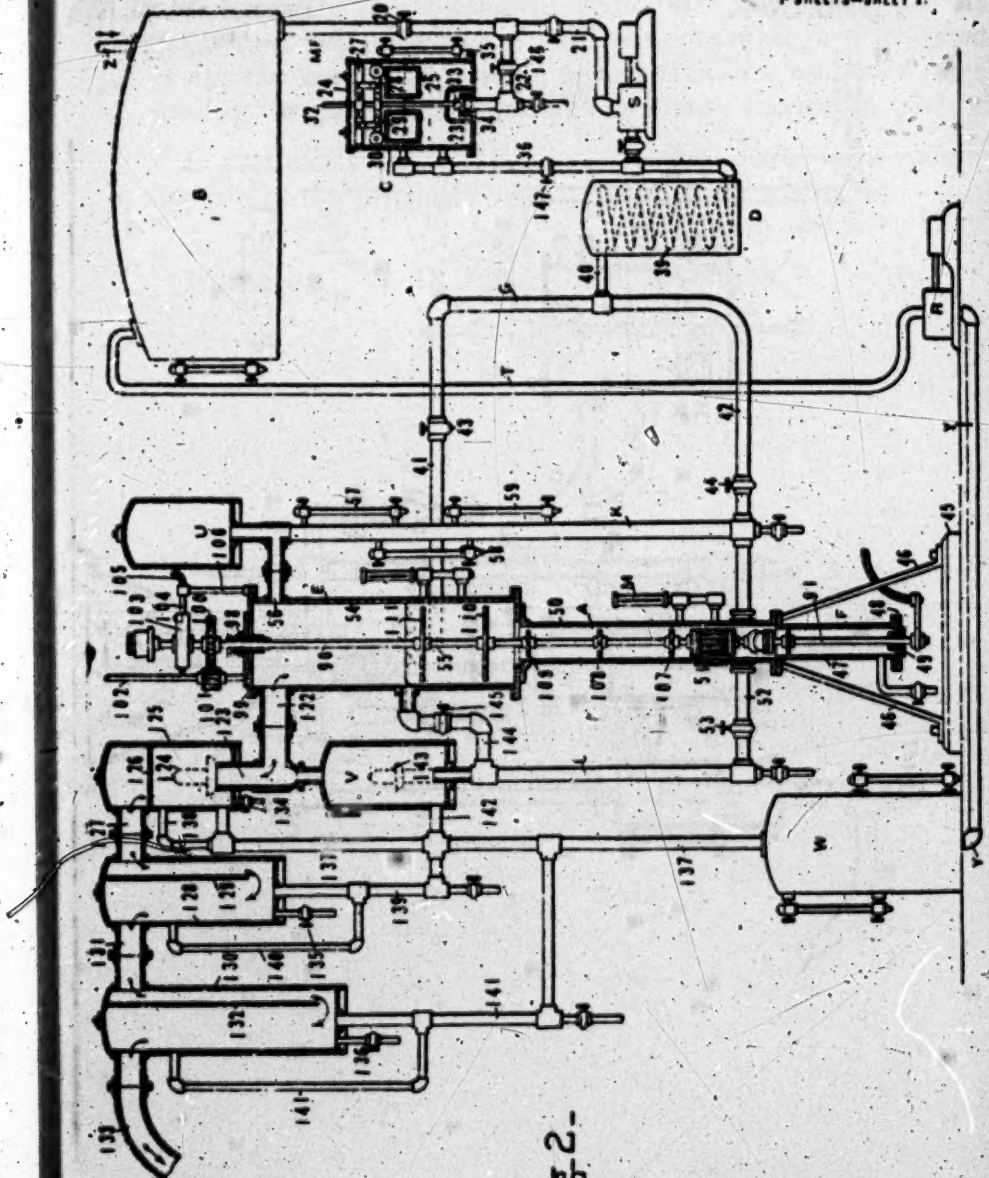

Fig. 2.

WITNESSES

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[fol. 1221]

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OIL CONVERTING APPARATUS.

APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

7 SHEETS—SHEET 3.

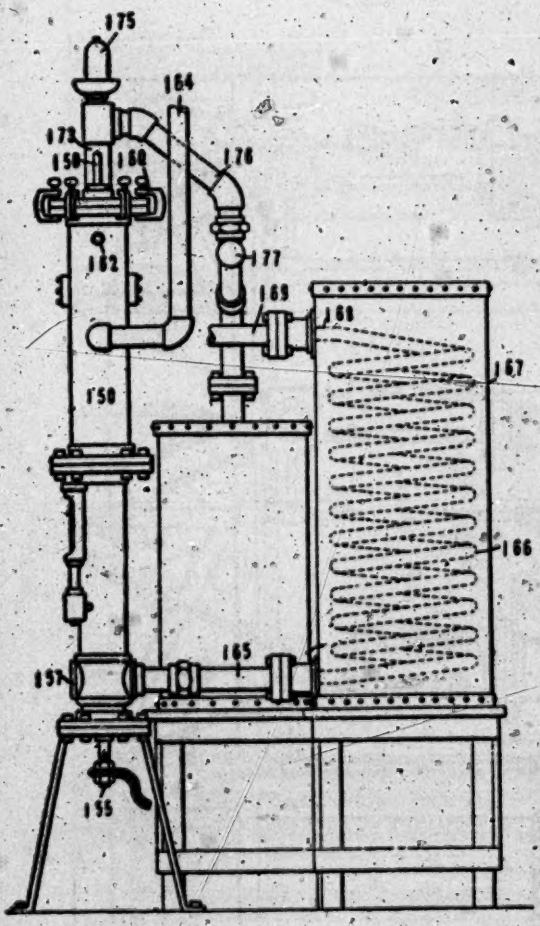

Fig. 4.

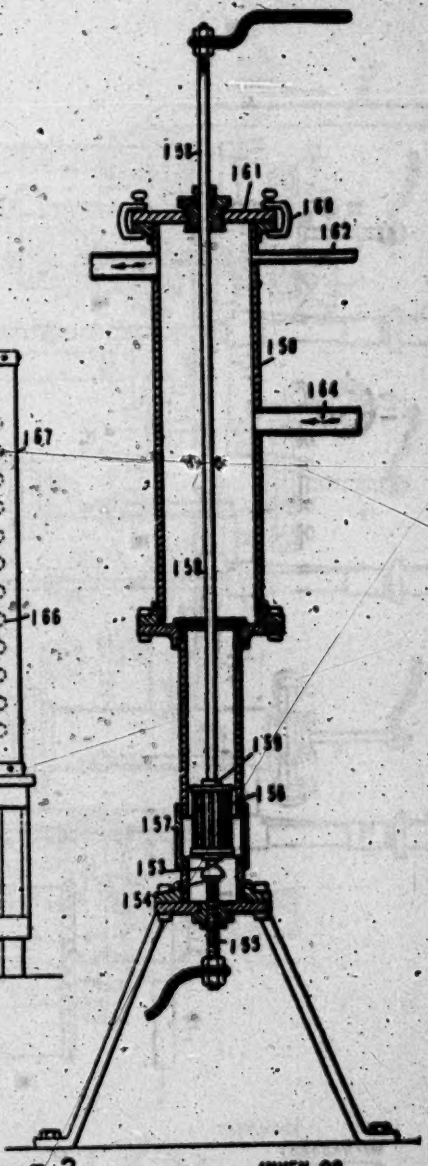

Fig. 3.

WITNESSES

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[fol. 1222]

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OIL CONVERTING APPARATUS.

APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

7 SHEETS—SHEET 4.

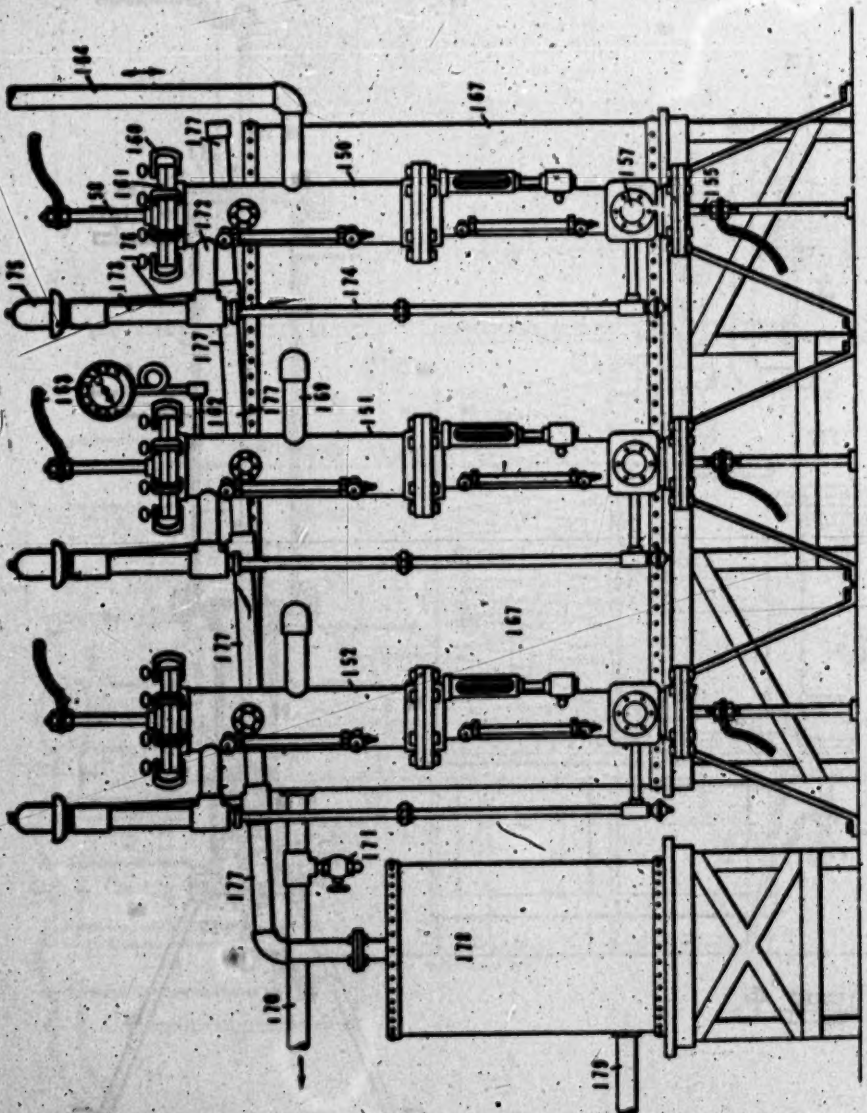

Fig. 5.

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[fol. 1223]

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APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

3 SHEETS—SHEET 3.

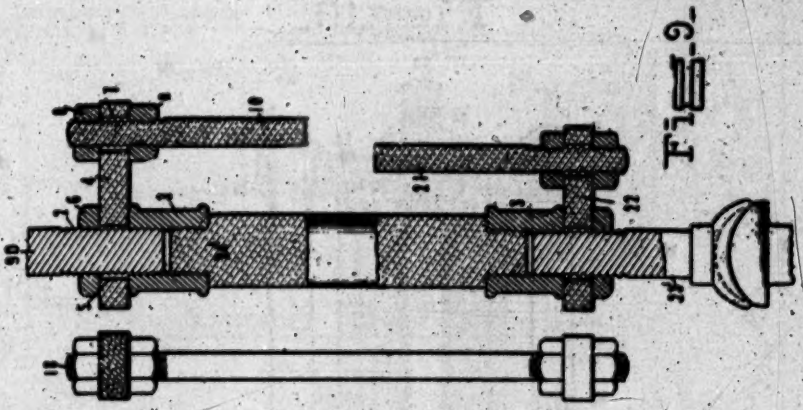

Fig. 6.

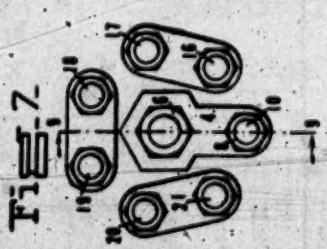

Fig. 7.

Fig. 8.

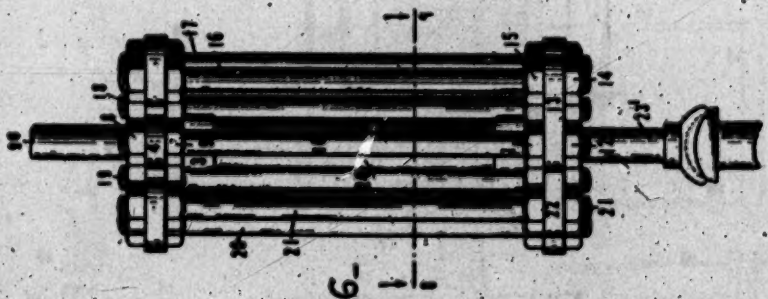

Fig. 9.

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[fol. 1224]

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OIL CONVERTING APPARATUS.

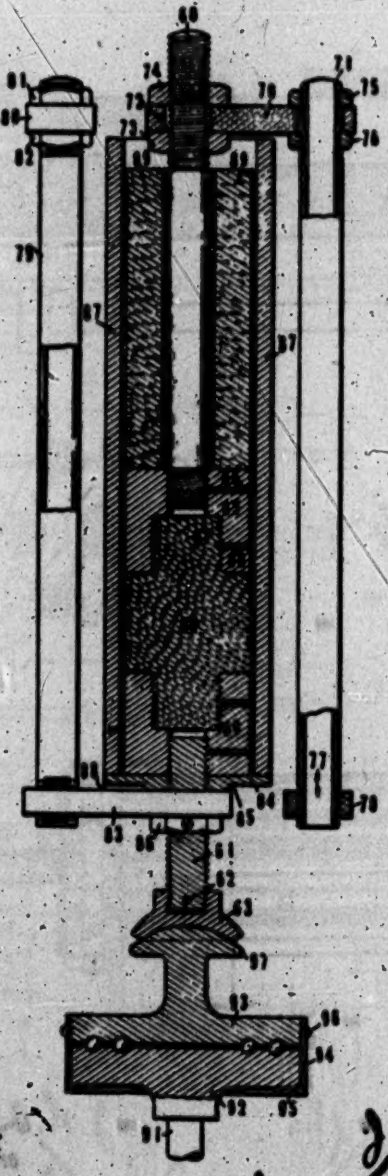
APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

7 SHEETS—SHEET 6.

Fig. 10.



WITNESSES:

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[fol. 1225]

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OIL CONVERTING APPARATUS.

APPLICATION FILED DEC. 1, 1909.

1,320,354.

Patented Oct. 28, 1919.

7 SHEETS—SHEET 7.

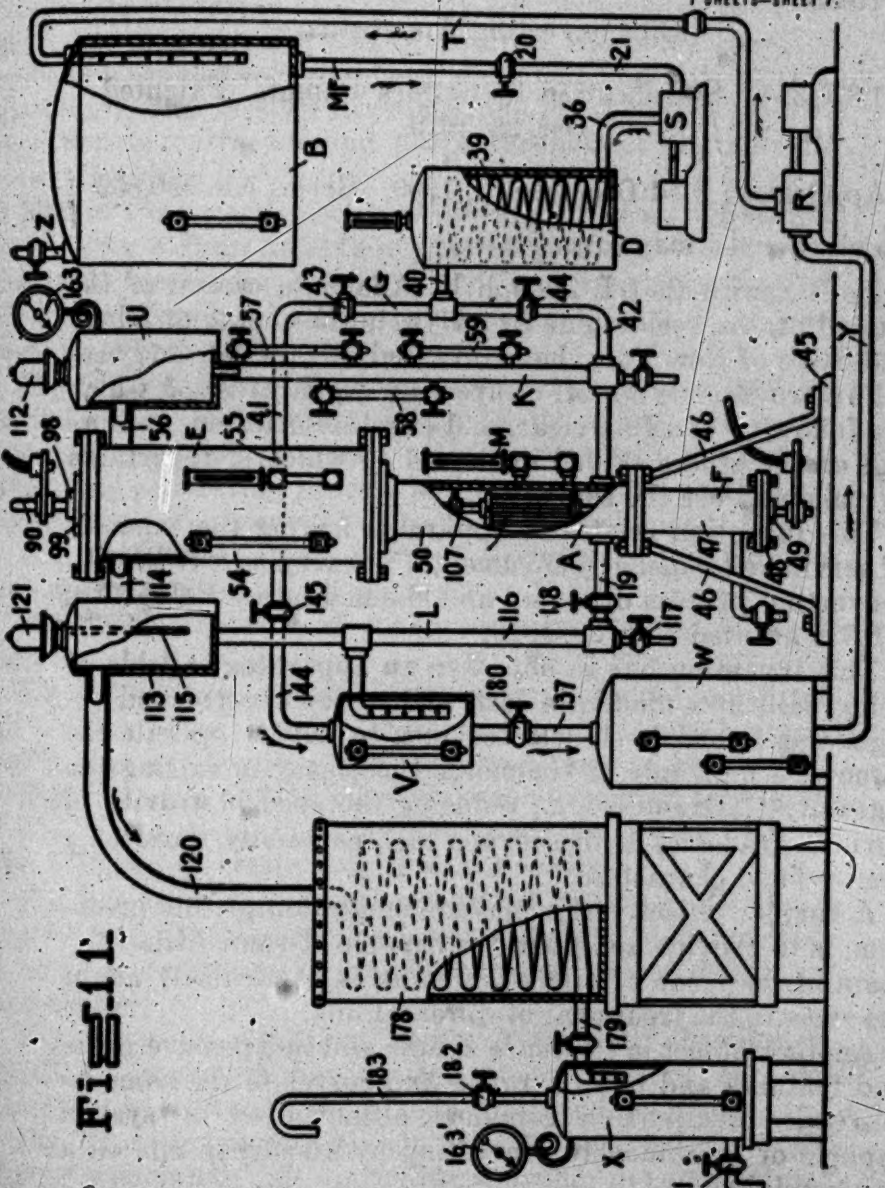

Fig. 1.

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INVENTOR.

BY Joseph H. Adams

ATTORNEY.

[fol. 1226] United States Patent Office

Joseph H. Adams, of Brooklyn, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Oil-Converting Apparatus

1,320,354. Specification of Letters Patent. Patented Oct. 28, 1919

Application filed December 1, 1909. Series No. 530,852

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Oil-Converting Apparatus, of which the following is a full, clear, and exact description, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to apparatus having the capacity of serving as a means instrumental in carrying out the oil-converting process disclosed and claimed in my Patent No. 976,975 granted Nov. 29, 1910.

This invention has in objective an apparatus capable of being built at a moderate cost, and so constructed and designed as to enable skilled workmen to readily operate the same at a high rate of commercial efficiency in raising the "gravity" (Baumé), i. e., reducing the specific gravity of various grades of hydro-carbon oils, especially those of a semi-refined character.

A further object within the contemplation of this invention, is to provide an apparatus capable of some little variation in the mode of operation so as to particularly adapt the same to the treatment of different oils.

Another object is to secure simple and inexpensive parts and features and to so arrange and correlate the same as to render available a complete organization or system capable of continuously converting hydro-carbon oils on a commercial basis.

Other objects will be in part obvious from the annexed drawings and in part pointed out hereinafter.

The invention accordingly consists in the features of construction, combinations of elements and arrangement of

parts which will be exemplified in the construction hereinafter set forth, and the scope of the application of which will be indicated in the following claims.

In order that this invention may be the more fully disclosed and otherwise made wholly comprehensible to those skilled in this art, drawings typical of the many possible embodiments thereof have been appended as a part of this disclosure, and in such drawings like characters of reference denote corresponding parts throughout the several views of which:

Figure 1 is a partly sectional illustration of an apparatus embodying certain aspects of this invention in which non-rotatable electrodes are employed, and also showing the structural details of an automatic feed typical of an element of this system.

Fig. 2 is a more complete representation of a system composed of coöperating elements including a moving heater and having the capacity of continuously subjecting oils to my converting process and providing for an efficient retreatment of unconverted fractions of such oils.

Fig. 3 shows a simple form of converter which may be used as an element of my apparatus.

Fig. 4 illustrates said converter connected with other parts.

Fig. 5 illustrates a series of converters adapted to subject oil to the successive action of my high-temperature heaters.

Fig. 6 is an elevation of a preferred form of heater.

Fig. 7 is a top or plan view of the device shown by Fig. 6.

Fig. 8 is a section looking downward along line 8—8 of Fig. 6 showing certain details more clearly.

Fig. 9 is an enlarged section taken at its upper end along line 9—9 of Fig. 7 and at its lower end along 9^a—9^a of Fig. 8, so as to render more apparent the structural details of this device.

Fig. 10 is an elevation, partly in section, showing in detail an improved construction of the electric core or heater in which tubular electrodes are used, and

Fig. 11, is an elevation view of the assembled construction of a complete unit apparatus showing, in combination, the principal necessary correlated parts from the oil supply to distillate collecting tanks at opposite ends of the system.

The reservoir tank—this is indicated on the drawings by the character B, and is, of course, to be taken in a purely

conventional sense. This reservoir is filled with fresh supplies of the oil to be treated by means of a pipe Z, and also [fol. 1227] with unconverted fractions by a suitable return pipe T, and the oil is drawn therefrom by means of the main feed pipe MF, having a suitable valve 20. This main feed pipe may have a branch 21 (as shown in Fig. 2) communicating with the cold oil pump S, and is also in communication with an automatic float feed device C by means of branch line pipe 22.

The automatic float feed C.—The purpose of this device is to eliminate so far as possible the necessity of alertness and personal skill on the part of the operator in insuring that the oil to be treated shall be brought within the radius of action of the electric heater in proper quantities and without unduly varying the level of the oil above said electric heater. It may here be stated that in operating an apparatus of this character the action of the electric heater is often so violent and produces such disturbances in the rate of flow and positions occupied by the oil as to necessitate close vigilance on the part of the operator, but by means of the automatic float feed it is proposed to do away with the necessity of quickly closing or opening this or that valve to maintain the oil at the desired level.

The form of automatic float feed shown by the drawings will suffice to render the essentials thereof comprehensible to others. Such device comprises a closed receptacle 23, preferably provided with a removable cover 24 to enable the working parts to be inspected. Within this circular closed tank is an annular hollow float 25 providing a central well 26. From an upper stationary cross-bar 27 (in which a valve stem is slidably journaled) there depends one or more brackets 28 to the lower ends of which are pivoted levers 29 having weights 30 at their outer ends. The other ends of said levers 29 are pivoted to a collar 31, which is fixed to the valve stem 32, so that when the pivoted ends of said levers 29 rise through the fall of their outer weighted ends, the valve stem 32 will be lifted. The weights 30 may be in the form of rollers rotatively carried by the outer ends of levers 29 and normally supported by the annular float 25, so that as this float rises with the inflow of oil the weights will be lifted, resulting in the depression of the valve stem 32. At its lower end, such valve stem carries a suitable valve, such as the puppet 33, which co-acts with

a valve seat 34, which in turn, is in communication with the inflow pipe MF. A gage glass 35 may be provided to give visual information as to the height of the oil in the automatic sight feed.

Preferably, a pipe 36 providing two branches 37 and 38 is used to withdraw the oil from the tank 23, the branch 37 being located uppermost and entering such tank 23 at a point coplanar with the predetermined level of the oil. The lower pipe 38 takes into the tank 23 below the level of the oil.

The oil preheater D.—Inasmuch as it is desired to conserve heat energy as much as possible in this apparatus, the comparatively cold oil flowing through the pipe 36 is preferably caused to pass through the oil preheater D and thus be raised in temperature before passing into the oil converting receptacle. This preheater may be of any suitable type but preferably provides a continuously rising coil 39 connected with the outlet pipe 40 which is located at the top so that any air bubbles may readily escape and not form air-locks in such preheating coil. The source of heat for said preheater may be the oil returning from the condensers and hot oil receivers at the other end of the apparatus or it may consist of any other heat supplying means.

The oil converting receptacle.—This composes that portion of the system in which the process of conversion is carried out and in this instance embodies an electric heater contained within a suitable receptacle and otherwise related to various operating and controlling adjuncts. The electric heater itself will be subsequently described. The receptacle shown by Fig. 2 provides a retort and converting chamber A, an underlying chamber F for receiving the heavy bottoms, and an overlying vapor dome E. The means for admitting oil to the conversion receptacle is shown as a piping G having an upper inlet or branch line 41 taking into the vapor dome E, and a lower inlet or branch line 42 taking into or below the retort A. The outlet pipe 40 from the preheater communicates with the piping G and by means of valves 43 and 44 the oil may be caused to flow directly into the upper dome E or into a lower part of the receptacle, as may be desired. The conversion receptacle may be supported from a suitable base 45 by means of supports 46 and will preferably consist of a number of sections bolted together in fluid tight connections.

Thus the heavy bottom chamber F is formed of a pipe-like section 47 having a bottom plate 48 providing an insulating bushing 49 tightly fitted in a central aperture. This bushing in turn tightly encircles a vertical conductor and insulates the same from the metal of the receptacle. The overlying retort chamber may also consist of a pipe-like section 50 having a sight 51 in its side opposite the electric heater so that the action of the latter may be observed. A suitable thermometer M may be arranged in permanent relation with the chamber A so that the temperature of the oil therein may be kept under constant observation. As has been stated, the branch line feed pipe 42 may enter the retort, as shown, and also a branch line pipe 52 having a [fol. 1228] valve 53 may connect such retort with a return pipe L to enable a flow to take place as will be subsequently described.

The vapor dome E comprises a pipe-like section 54 having an inlet at 55 for the oil from the branch pipe 41 and preferably also providing a connection 56 for the gage column pipe K. This pipe K connects at its lower end with the retort chamber A through the branch line 42 and is also permanently connected with the vapor dome through the pipe 56. This gage column provides the sight gages 57, 58 and 59, which show the level of the oil in the vapor dome. It has been found from experience that by using a gage column K having the sight gage glasses connected directly with the same, instead of with the conversion receptacle, that more positive and uniform readings are obtainable. Under the intense action of the heater, the oil in the conversion receptacle is at times greatly agitated, thereby producing a corresponding disturbance in the gage glasses, which, under such circumstances, tends to give misleading readings. The action of the gage column K is materially improved by providing the upper end thereof with vapor expansion chamber U. The said oil converting receptacle contains the heater which is preferably electrically operated so as to enable high temperatures to be positively maintained in members directly contacting with the oil and oily vapors to be treated.

The electric heater.—This invention proposes to intimately subject the oil to temperatures which, in comparison with any heretofore commercially used, are exceedingly high, and since this treatment, because of the volatile and

inflammable character of the oil, presents many practical difficulties, the precise nature of the electric heater will now be described in detail, thereby imparting to those skilled in the art such a full understanding of this embodiment as will enable them to diversely formulate this invention to meet special conditions.

Any metal such as copper or its alloys having high electrical conductivities and capable of withstanding the action of a contact with oil while at moderately high temperatures, may be used for the construction of the supporting and current-conveying parts, but extensive experimentation has shown that comparatively few commercially available materials are wholly suitable for composing the resistance or heating members. Of such materials, the substance known as "graphitic carbon" is preferred. This easily obtainable substance is an artificial form of carbon made by an electrical process and is used to a considerable extent as a substitute for ordinary carbon or graphite in electric furnace work. This graphitic carbon is very homogeneous and non-amorphous in structure and somewhat resembles ordinary graphite, but is somewhat softer, less lustrous, and much better able to withstand excessive temperatures without cracking or otherwise disintegrating.

The electric heater will comprise a member composed of this or other suitable available material and such member or members may assume the form of a rod or rods such as that indicated by 10 of Figs. 6-9. Preferably, the electric heater comprises a circumferential series of such resistance rods or pencils, fastened together in pinion-like fashion to form a grid, and so connected that current may flow through the same at the best advantage. While the precise manner of connecting to these resistance rods may, of course, be varied to conform to the various available currents and to meet other conditions, the specific form shown by Figs. 6 to 9 inclusive will be found very suitable in most instances. This electric heater is adapted for working under an electric current having a relatively low voltage and an accordingly high amperage, which current is brought in by means of a metallic conducting rod 90. The end of such conductor 90 may be provided with screw threads 2 at its extremity preferably threaded into an internally threaded collar 3. A link 4 of massive proportions has an aperture

5 which circumscribes the end of the conductor 90, as shown, and a nut 6, which, like the collar 3, is preferably composed of metal, operates to securely clamp the link 4 in place and at the same time establish its electrical connections with the conductor 90. This link 4 is preferably composed of graphitic carbon and is sufficiently massive to convey current without its becoming unduly heated by such current. The object of utilizing this link in this way is to provide some means for connecting the conductor 90, which is unable to withstand excessive temperatures, with the resistance rod, which is intended to be normally maintained at such high temperatures. This link 4 serves admirably in this capacity and at its outer end it provides an aperture 7 through which passes the end of one of the resistance rods. The resistance rod 10 is sufficiently small in cross-section to be raised to a very high temperature by the current passing through the apparatus, and is provided with screw threads near its end. A nut 9 is in screw-threaded relation with the rod 10 and bears against the lower face of the link 4 while the nut 8 has a similar construction with respect to the rod 10 and clamps down against the upper surface of the link 4. By screwing these rods together [fol. 1229] fairly tightly, the several parts will not only be sufficiently positioned, but will also be efficiently connected electrically with the conductor 90. It may here be stated that link 4, the nuts 8 and 9, and the rod 10 are all preferably composed of the above mentioned graphitic carbon, which it has been found can be readily machined and which possesses sufficient strength to provide an amply strong structure. At its lower end, rod 10 is electrically connected by means of nuts 11 and 12 with the link 13, which extends circumferentially for a short distance and is connected in a counterpart manner by nuts 14 and 15 to the rod 16. At its other end, said rod 16 is similarly connected with rod 17, and in like manner the rods 17, 18, 19, 20 and 21 have their adjacent ends electrically connected in the manner described. The last-mentioned rod 21 is connected with a conductor of opposite polarity 23′. In order to insulate and also separate 90 and 23′ against relative movement without imposing unnecessary strain on the somewhat fragile resistance grid or heater, this invention also proposes

a comparatively massive column 24′ of non-conduction heat-enduring material such as soap-stone or the like. This intervening column may be screwthreaded or otherwise attached to conductors 90 and 23′.

The movable electric heater.—This heater is shown by Fig. 10 and merely constitutes a modified form of the stationary heater above described. The features of construction, wherein this modified heater differs from the stationary form enable a due amount of heating material to be brought into intimate contact with greater amounts of the oil to be converted. This is done by causing the electrodes to have a comparatively rapid movement while submerged in the oil and is also accomplished by giving one or more electrodes a tubular form and causing oil to pass through the bore of such tubular electrodes. This modified construction is embodied in the system set forth in Fig. 2, but the specific construction of the electric heater will be described in connection with Fig. 10 which shows the same in greater detail. The one terminal of this electric heater is designated by the character 60 and consists of a rod of copper or other material having a high electric conductivity, which rod is provided with screw threads at its upper and lower ends, as shown. The other terminal consists of a rod of similar material 61, screwthreaded throughout its length, and preferably having affixed to its lower end by means of the screw threads and a set screw or pin 62 a detachable section 63 of a ball and socket joint. Inasmuch as it is desirable that the two terminals 60 and 61 shall be insulated from one another, (except through the electrodes), and shall be held together in a rigid relation enabling them to move as a unit, this invention proposes an intervening section 64 composed of soapstone or other heat-enduring, insulating material and attached at opposite ends to the two terminals 60 and 61. A convenient expedient for fastening these members together consists in a collar 65 having a screwthreaded aperture adapted to receive the lower screwthreaded end of the terminal 60 and locked against rotation by means of a set screw 66, and also having an enlarged screwthreaded aperture adapted to receive a threaded end 67 of the soapstone interponent 64, and also located in place by means of a set screw 68 at the other end.

A counterpart collar 69 may couple the interponent 64 and the terminal 61. At the upper screwthreaded end of the terminal 60, a link 70, preferably of graphitic carbon, electrically connects such terminal 60 with the first electrode 71 of the series. It being desirable that the link 70 shall be adjustable as to position for reasons hereinafter appearing, it may have an aperture 72, enabling it to freely pass over the threaded upper nut of the terminal 60, and securely fastended thereto in any desired vertical position by means of the lock nuts 73 and 74. At its other extremity, the link 70 has a corresponding connection with the electrode 71, being affixed thereto in the desired relation by means of the nuts 75 and 76 which are preferably composed of infusible material such as graphitic carbon. It will be noticed that the electrode 71 is tubular, thus enabling the oil to be converted to uprise through the same as shown by the arrow 77, and in this way increase the converting capacity of the electrode 71 by enabling oil to contact therewith internally as well as externally. At its lower end, this electrode 71 is connected with a link 78, and, for the sake of simplicity, this may be done by directly screwthreading the lower end of the electrode 71 into a screwthreaded aperture of the link 78. It is preferable, however, to use the nuts at the other end of the electrode so that any inequalities in length may be easily compensated for by means of the lock nuts and thus prevent undue strains caused by any slight inaccuracies in the proportions of the parts. The successive electrodes will be connected together in a corresponding manner, using lock nuts at the one end and direct thread connections at the other end. 79 illustrates the last electrode of the series which receives the current from its preceding companion by means of the link 80 positioned by the lock nuts 81 and 82 and is connected with the other terminal 61 by means of the link 83 with which it is preferably directly connected as described. The terminal 61 carries a supporting collar 84, which, being screwthreaded thereto, will not undergo displacement relatively to the terminal 61. The link 83 presses against a hub-like portion 85 of the supporting collar 84 and is held in place by means of a nut 86 screwthreaded to the terminal [fol. 1230] 61. This structure possesses the advantage that in case the line 83 should become fractured, it may be easily

replaced removing the section 63, and then unscrewing the nut 86.

In order to protect the terminals 60 and 61 from the intense heat of the incandescent electrodes and at the same time to restrict the flow of oil to the immediate vicinity of the electrodes, this invention proposes a heat-insulating shell 87 which may assume the form of a porcelain tube. This tube 87 rests directly on the supporting collar 84 and is thus supported in such a way that its weight is not carried by the electrodes. Because of the fact that the circumferential portions of the collar 84 are slightly distanced as indicated by 88 from the link 83, such link 83 is protected from bending strains which might otherwise occur and cause fractures thereof. The length of the porcelain 87 is such as to fall slightly short of the upper links 70, 80, etc., and its internal diameter is preferably only slightly larger than that of the soapstone interponent 64 and the collars 65 and 69. The remaining space is taken up by the tubular member 89 which is a bore of such size as enables it to be readily slipped over the terminal 60, as shown by Fig. 10. This tubular member 89 will preferably be composed of some suitable asbestos-containing, heat-insulating material, having the capacity of enduring considerable temperatures.

Inasmuch as it is desired to rotate the electric heater shown by Fig. 10 through the vertical conductor 90, which is, in turn, driven by means hereinafter to be described, this invention also proposes to support the lower end of the electric heater on one or more rotatable bearings capable of carrying the heavy currents which are necessary to maintain such heater at its high temperature. A simple and satisfactory form of such bearing may be formed by non-rotatably supporting the conductor 91, in the bottom plate 48 of the section F of the oil-converting receptacle, by means of a suitable oil-tight bushing 49. The upper end of this conductor 91 terminates in the collar 92, forming a section of a ball bearing, as shown by Fig. 10. The complementary section 93 of this ball bearing, preferably carries an annular retainer 94, having an inturned flange 95 bearing against the collar 92 and is detachably secured to the upper section 93 by means of screws 96. The upper section 93 carries a portion 97 having a spherical upper sur-

face closely interfitting with the spherically concaved seat provided by the lower surface section 63. This construction enables the electric heater to be easily removed as a unit by uplifting the same by means of the conductor 90, since the sections 63 and 97 may easily be separated and, because of their interfitting construction, they may be readily brought together by simply lowering the electric heater until the section 63 contacts with the section 97 and automatically assumes a close fit therewith, as will be readily understood. The conductor 90 is journaled in a gas-tight bushing 98 carried by the removable top plate 99 of the vapor dome E. The object of making this plate 99 removable is to enable the parts to be withdrawn whenever an undue quantity of carbon has been deposited on the electrodes, or whenever for other reasons it is desirable to replace or clean parts thereof. The conductor 90, which has a driving, screwthreaded connection with the upper end of the terminal 60, is, in turn, driven through the gear 100, which gear is impelled by a driving pinion 101, mounted on the driving shaft 102. One of the other of these gears, or both, may be constructed of fiber or other insulating material or may be insulated by means of fiber bushings. The conductor 90 is electrically connected with the generator by means of a commutator and bushing 103 and 104 to which the current is led by means of a conductor 105, carried by a support 106, so as to be insulated from the receptacle E. To prevent an undue agitation of the oil within the receptacle, during the process of conversion, and to insure a steady and uniform flow of such oil, a series of apertured baffle plates 107, 108, 109 and 111 may be mounted on the conductor 90.

Many of the features of construction set forth in the foregoing may be used without others, thus, as shown in Fig. 1, the device may assume a modified form in which the electric heater is stationary instead of being rotatable. In this case the ball bearing may be dispensed with though preferably the self-seating sections 63 and 97 will be used to enable the heater to be readily withdrawn and replaced without any difficulty and at the same time insuring good electrical connections. The conductor 90 shown by Fig. 1 may also provide perforated baffle plates 107, 108, 109 and 110, as shown. In the simple arrangement shown by Fig.

1; gage column pipe K may provide a pop valve 112 at its upper end, in lieu of the expansion chamber U shown in connection with Fig. 2 or as shown in Fig. 11, the release pop valve 112, may be mounted at the top of tank U.

Apparatus for collecting and returning heavy unconverted oils.—It may here be stated that since the process of conversion depends upon subjecting oil or oily vapors to very high temperatures considerably above their va- [fol. 1231] porizing points, and since this evidently cannot be done without volatilizing in unconverted form large quantities of such oil, it will be necessary to retreat such fractions as have escaped the action of the process. By arranging the electrodes in the manner described, it is possible to materially reduce the escape of unconverted oils, but nevertheless, it has been found that considerable quantities pass through the converting receptacle without having been materially affected. Such oils, being comparatively heavy, may be readily condensed or caught by properly arranged baffle plates, and to this end this invention proposes a structure or system of parts intervening between the condenser for the converted fractions and the oil-converting receptacle. Turning now to Figs. 1 and 11 wherein is shown a simple construction of this character, 113 denotes a hot oil tank connected with the vapor dome E of the converting receptacle by means of pipe 114. The oily vapors and particles of heavy oil carried thereby, pass through this pipe 114 and project against the baffle plate 115 and this action results in the precipitation of considerable quantities of the heavy oil. This oil collects in the tank 113 and may be withdrawn from the same by opening the cock 117 in the pipe 116 or may be returned directly to the action of the electric heater by opening the cock 118 in the return pipe 119. Such vapors as have escaped condensation in the tank 113 pass through the pipe 120 to a suitable condenser capable of condensing all products which may have a liquid form at ordinary temperatures. A pop valve 121 is preferably provided in this form of the apparatus to insure safety in case the pressure should become excessive.

Returning now to Fig. 2, there will be seen a comparatively more efficient form of this apparatus capable of handling the oil to a better advantage on a commercial basis.

The oil vapors super-saturated with more or less of the unconverted comparatively heavy oils and also carrying minute particles of the same, pass out of the vapor dome through the pipe 122, and thence up through the short riser 123 and by the pop valve 124 into the expansion and condensing dome 125. While expanding, considerable quantities of the heavy untreated fractions will be precipitated and caught by the perforated baffle plate 126 and returned to the bottom of the expansion tank 125. The vapors, which may still be charged with quantities of unconverted oil, then pass through pipe 127 into the vapor trap 128, wherein a still further precipitation may obtain through the contact of such vapors with the perpendicular baffle plate 129. The vessel 128 is preferably slightly larger than tank 125 and may in turn be connected with a counterpart but still larger vessel 130 by means of the pipe 131. The major portion of the remaining unconverted fractions of the oil will be precipitated by the baffle plate 132 so that the oil which finally passes out through the pipe 133 will display a gravity materially higher on the Baumé scale than the portions originally admitted to the action of the electric heater. The pipe 133 leads to a suitable condenser which may assume any of the forms commercially available.

Each of the tanks 125, 128 and 130 is preferably provided with drain pipes controlled by valves 134, 135 and 136, so that samples of the oil collected in such tanks may be directly obtained. A system of piping is also employed to return the accumulated heavy oils to the main reservoir tank containing the fresh supplies of oils to be treated. Thus, a pipe 137 connects directly with the lower portion of the tank 125 and preferably also provides an emergency branch line 138 connecting with the upper portion of said tank. This pipe leads directly to a receiving tank W, which is, in turn, connected with a hot oil pump R by means of a return pipe Y, and the pump R is connected with a reservoir tank B by means of a pipe T either directly, as shown, or indirectly through the pre-heater D, so that the heat in the returned oil may be utilized in raising the temperature of the pre-heater. In like manner a pipe 139 connects the bottom of the tank 128 with the tank W and provides an emergency branch line 140 and a pipe 141 connects the

lower part of the tank 130 with the tank W and may also provide a similar emergency branch line 141.

The oil carried over through the pipe 122, and precipitated during its flow through the short riser 123, flows back into the hot oil tank V and thence into the return pipe 137 through the outlet 142. This tank V contains a puppet 143, which is mounted at the upper extremity of of the pipe L, which pipe is connected at its upper end with the vapor dome E at the level of the oil therein, through the branch line 144 and at its lower end with a retort A through the branch 52. Valves 53 and 145 enable the flow of oil through these pipes to be controlled.

Mode of operation.—This apparatus may be operated by gravity with the oil flowing either upwardly or downwardly past the electrodes, or it may be operated under high pressure with a corresponding alternativeness in the flow of the oil. Thus, when operating by gravity, with a down flow of the oil, certain valves are open and others closed, as will be understood, so that the oil therein from the reservoir tank B passes down the main feed pipe MF through the automatic feed regulator thence through the pre-heater [fol. 1232] D and into the pipe G. Valve 44 being closed and valve 43 being open, the oil will flow through the branch 41 and into the receptacle E at point 55. Valve 145 being closed, such oil will flow down past the electric heater out through the pipe 52, up through the pipe L, into the tank V and thence into the receiving tank W. The vapors will pass through the parts described in the foregoing paragraphs.

In case it is desired to have the flow upwardly past the electrodes, the valve 43 will be closed and 44 opened, thus admitting the oil to the lower section A and forcing it upwardly into the vapor dome E, the valves 53 being closed. The vapors, &c., will rise through the pipe 122 and the liquid oil flow out through pipe 144, the valve 145 being open, and into the tank V and then into the receptacle W, from which it may be returned to the main reservoir B by means of the pump R. In case it is desired to act upon the oil under heavy pressure, valves 146 and 147 will be closed to cut out the automatic float feed (Fig. 2) and the pump S will be put into operation to draw off oil from the reservoir B and force the same under heavy pressure

through the pre-heater D. Dependent upon the adjustment of the valves 43 and 44, the oil may be caused to flow either upwardly or downwardly past the electric heater 51. In this connection it is to be noted that the pop valves 124 and 143 not only control the pressures but also act as safety valves, for whenever the pressures become excessive one or the other or both of these valves will open and permit the vapor and the fluid oil to escape into the return parts of the system. Valve 143 is so positioned and tensioned as to maintain the level in the receptacle E in the position desired.

It will be clear that the oil supplied from the oil reservoir may have a substantially fixed rate of flow to and past the heater. This substantially constant relative movement of the oil and heater may be changed by the rate of conversion of the heater for if the rate of conversion becomes greater the rate of flow will correspondingly increase. This acceleration in the rate of flow of oil is adapted to be controlled by the automatic regulator which is intended to keep a practically constant depth of oil in the converting chamber. Again, it will be obvious that the relative movement between the electric heater and the oil may be also accelerated by the rotation of the electric heater.

In the forms illustrated in Figs. 1, 5 and 11 where the condenser is shown in free communication with the converter the pressure in the converter will of course extend throughout the condenser and therefore in order to maintain the pressure it is necessary to have some closure for the system beyond the condenser. Such a closure will be understood by those skilled in the art as existing in the pipe 179 beyond the point where that pipe is broken away, in Fig. 5, and such closure is illustrated in Fig. 11 as consisting of a valve 181 in the liquid discharge outlet and a valve 182 in the gas pipe leading from tank X. It will further be understood by those skilled in the art that the generation of vapors in the converter will cause pressure and consequently make it necessary to use a pump or other means for forcibly feeding the oil into the system continuously.

Figs. 3, 4 and 5 illustrate another form of this invention suitable for the treatment of various grades of oil by caus-

ing the oil to first pass through a preliminary converter, then through a suitable cooling coil and thereafter through one or more retreating converters and cooling coils. Thus, as shown, the oil may successively course through a series of three converters 150, 151 and 152 freely connected one with another by means of vapor line 177, and thus successively undergo an alteration in character until the final desired quality is imparted to said oil. Fig. 3 represents in cross section the construction of a very simple form of converter such as those in Figs. 4 and 5. This form is to be regarded as typical in these figures as any of the above disclosed more important forms may be employed. In this form the electric heater has its lower terminal 153 detachably connected with the lower leading-in conductor 155 by means of a self-seating joint 154 such as that described in connection with the other forms. The electric heater 156 is positioned opposite sight-glass 157 in the lowermost narrow portion of the converting receptacle and the conductor 158 leads upwardly from the terminal 159 as described in the foregoing description. This conductor 158 is detachably secured to the upper terminal 159 of the electric heater but the connection is such that the heater may be raised out of the receptacle by withdrawing the conductor after removing the clamps 160 which hold down the cover-plate 161 of the upper end of the converting receptacle. One or more of these receptacles may be provided with a pipe 162 leading to a pressure gage 163 so as to enable the operators to be constantly informed as to the pressure under which the apparatus is working.

In operation, the oil to be treated enters through the pipe 164, then flows into the vapor dome, thence downwardly into the retort past and into intimate contact with the incandescent electrodes of the heater, and thence out through pipe 165 (see Fig. 4), into the lower end of the coil 166 of the cooler 167. By entering at the lower end of this coil, the oil and gases are able to rise therethrough [fol. 1233] without interruption and without the likelihood of forming air-pockets. The upper end 168 of the coil 166 is connected with a pipe 169 leading into the next converter 151 of the series. The oil then passes down through the incandescent converter past the incandescent electrodes thereof, into a second cooling coil, then into a third retort,

etc. Ultimately, the oil passing through the series emerges from the last cooling coil through a pipe 170 preferably provided with one or more draw-off cocks 171 and from this it may be returned to the beginning of the series if desired.

Returning now to the first converter, the course of the vaporized products may be followed. The major proportion of the vapors evolved in the first converter 150 will rise through the vapor dome and out through the pipe 172 at the upper end of such dome. The vapors must then rise a short distance through the stand-pipe 173 and the precipitated unconverted residues may flow back through the pipe 174 and return to the action of the electric heater. The vapors that rise through the stand-pipe 173 pass by the release pop valve 175, which will be operative in case the vapor pressure unduly increases, and then will flow downwardly through the elbow pipe 17 into the inclined vapor main 177. The successive converters are connected in like manner and discharge their converted product into the inclined main 177 which leads to the condensing apparatus 178 and from which the converted product may be withdrawn through the pipe 179.

As many changes could be made in the above construction and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the language used in the following claims is intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween.

Having described my invention what I claim as new and desire to secure by Letters Patent is:

1. An apparatus of the nature disclosed, comprising in combination, an oil tank, a receptacle connected therewith, an electric heater arranged in said receptacle, means for enabling oil to be maintained in said receptacle at approximately a predetermined level above said electric heater, and a pressure pump for accelerating the relative move-

ment between the electric heater and the oil contacting therewith when said heater is at an elevated temperature.

2. An apparatus of the nature disclosed, comprising in combination, an oil supply tank, a vertically elongated retort, an electric heater arranged in the lower part of said retort, piping intervening between said retort and said tank, an automatic oil feed device interposed in said piping to automatically open communication between said tank and retort when the level of oil in the latter lies below a predetermined level, and to automatically close said communication when said level is attained.

3. An apparatus of the nature disclosed, comprising in combination, an oil supply tank, a receptacle connected therewith, an electric heater arranged in said receptacle comprising a multiple of graphitic-carbon rods alternately and serially connected at their ends, a condenser in free communication with said receptacle and a liquid collecting tank at the foot of or beyond said condenser connected therewith; means for enabling oil to be maintained in said receptacle at a predetermined level above said heater and means for continually supplying oil to said receptacle to compensate for that withdrawn therefrom in liquid or vapor form.

4. An apparatus of the nature disclosed, comprising in combination, an oil tank, a receptacle connected therewith, an electric heater arranged in said receptacle, comprising a plurality of serially connected graphitic-carbon rods, means for enabling oil to be maintained in said receptacle at approximately a predetermined level above said heater when at an elevated temperature and means for supplying electric current to said heater for the purpose of raising the temperature of said oil to heat of sufficient intensity to crack and convert the same into oils essentially different from the original untreated oils.

5. An apparatus of the nature disclosed, comprising in combination, an oil tank, a receptacle connected therewith, an electric heater comprising a circumferentially arranged series of graphitic-carbon rods, terminals supported by said receptacle and electrically connected with said heater and serving to maintain the same at a fixed level with respect

to said receptacle, a pressure pump and valves for regulating the entry of oil to said receptacle whereby its level may be maintained at approximately a predetermined distance above said heater and means for maintaining vapor pressures in excess of atmospheric pressure within said receptacle to assist in the process of oil conversion.

6. An apparatus of the nature disclosed, comprising in combination, an oil tank, a receptacle connected therewith, [fol. 1234] an electric heater within said receptacle comprising a series of resistance rods, a plurality of links alternately connecting the adjacent ends of said resistance rods in series, electrical connections extending from the exterior of said receptacle to the terminals of said electric heater to enable a heavy electric current to pass through said resistance rods in order to maintain the same at an elevated temperature while submerged in the oil contained in said receptacle, a pressure pump for accelerating the relative movement between said electric heater and the oil contacting therewith, means for raising the temperature of said oil above its vaporizing points and means for maintaining superatmospheric vapor pressures within said receptacle.

7. An apparatus of the nature disclosed, comprising in combination, an oil supply tank, a receptacle connected therewith, an electric heater comprising a circumferentially arranged series of graphitic-carbon resistance tubes, terminals supported by said receptacle and electrically connected with said heater and serving to maintain the same at a fixed point within said receptacle; means for causing rotation of said tubular heater, a pressure pump and valves for regulating the entry of oil into said receptacle whereby its level may be maintained at approximately a predetermined distance above said heater, means for raising temperatures of oils above their boiling and vaporizing points and means for maintaining vapor pressures in excess of atmospheric pressure over the oil in said receptacle and in the condenser.

8. An apparatus of the nature disclosed, comprising in combination, a source of oil, a receptacle connected therewith containing a heater, a condenser in free communication with said receptacle, a pressure pump for forcing oil

from said source into said receptacle while oil contained therein is maintained under vapor pressure, means for subjecting oil in said receptacle while under pressure above atmospheric pressure, to the action of a member maintained at a temperature sufficient to raise the heat of contained oil in said receptacle to heat in excess of their vaporizing points.

9. In an apparatus of the nature disclosed, comprising in combination, a source of oil, a heating member and an inclosed oil containing receptacle in free communication with a condenser; a pump for forcing oil from said source into intimate contact, while under pressure above atmospheric pressure, with said heater while the latter is at an intense temperature; means for withdrawing and condensing under pressure vapors evolved from said containing receptacle.

10. An apparatus of the nature disclosed, comprising in combination, an oil supply tank, a receptacle connected therewith, an electric heater arranged in said receptacle comprising a multiple of graphitic-carbon rods alternately and serially connected at their ends, a condenser in free communication with said receptacle and a liquid collecting tank at the foot of or beyond said condenser connected therewith; means for maintaining high pressure in said apparatus, means for enabling oil to be maintained in said receptacle at a predetermined level above said heater and means for continually supplying oil to said receptacle to compensate for that withdrawn therefrom in liquid or vapor form.

11. An apparatus of the nature disclosed, comprising in combination, an oil supply tank and pump, an oil preheater and series of two or more tubular converters freely connected by a vapor line one with another and in free communication with a condenser, heaters contained within the tubular converters, a heater for raising temperatures of the supplied oils and means for continuously circulating oil through the apparatus under pressure for the purpose of converting high boiling oils into lower boiling products under the influence of intense cracking heats and superatmospheric pressures.

12. An apparatus of the nature disclosed, comprising in combination, an oil supply, heating means capable of being raised to incandescence, means for continuously feeding oil from said supply to said heating means, means for condensing and returning to the oil supply the unconverted high boiling point products and means for condensing the remaining vaporous products.

13. An apparatus of the nature disclosed, comprising an elongated retort of restricted cross section, means for continuously supplying oil under pressure to said retort, means for locally applying high heat to the restricted volume of oil in said retort to convert or crack the same, means for maintaining the generated vapors under pressure in contact with the surface of the oil in said retort and means for condensing the vapors.

14. An apparatus of the nature disclosed, comprising an elongated retort of restricted cross section, means for continuously supplying oil under pressure to said retort, means for locally applying high heat to the restricted volume of oil in said retort to convert or crack the same, means for maintaining the generated vapors under pressure in contact with the surface of the oil in said retort, means for collecting and returning to the source of supply portions of unconverted liquid carried by said vapors and means for condensing the remaining vapors.

15. An apparatus of the nature disclosed, comprising in combination, a closed chamber adapted to contain oil, means for heating the oil in said chamber to a cracking tempera- [fol. 1235] ture, means for continuously forcing oil into said chamber under pressure, a condenser in free communication with said chamber and means for maintaining pressure in said apparatus to and through the condenser.

16. An apparatus of the nature disclosed, comprising in combination, a retort embodying a pipe-like section, means for locally heating the oil in said pipe-like section to a cracking temperature, means for continuously forcing oil into said section under pressure, a condenser in free communication with said chamber and means for maintaining pressure in said apparatus to and through the condenser.

17. An apparatus of the nature disclosed, comprising in combination, a source of oil, a receptacle connected there-

with, and a heater combined with said receptacle adapted to be maintained at a cracking temperature in contact with the oil therein, an outlet for the oily vapors evolved by the action of said heat, a receptacle connected with said outlet and adapted to collect portions of the oily liquid carried by said vapors, means for returning said collected liquid to the action of said heater, and means for condensing the residual vapors.

18. An apparatus of the nature disclosed comprising in combination a plurality of oil converters, a condenser and means for maintaining pressure on the oil in said converters to and through said condenser.

19. An apparatus of the nature disclosed comprising in combination a plurality of oil converters adapted to furnish a vapor space above the oil therein, a condenser, means for connecting the vapor spaces of said converters with said condenser and with each other and means for maintaining pressure in said converters to and through said condenser.

20. An apparatus of the nature disclosed comprising in combination a series of oil converters, means for supplying oil under pressure to the first converter of the series, means for separating from the vapors generated the unconverted oil and for supplying that oil to the next converter of the series, means for taking off and condensing the converted vapors from said converters, and means for maintaining pressure on said vapors in the converters to and through the condensing means.

21. An apparatus of the nature described, comprising in combination, an oil supply tank, a vertically elongated retort, an electric heater arranged in the lower part of said retort, piping intervening between said retort and said tank, and an automatic oil feed device interposed in said piping to automatically open communication between said tank and retort when the level of the oil in the latter lies below a predetermined level, and to automatically close said communication when said level is attained.

22. An apparatus of the nature disclosed, comprising in combination, a source of oil, a receptacle connected therewith, a pressure pump for forcing oil from said source into

said receptacle under pressure, and means for subjecting the oil in said receptacle while under pressure to the action of a member maintained at an incandescent temperature.

23. An apparatus of the nature disclosed, comprising in combination, a source of oil, a receptacle connected therewith, means for maintaining oil under pressure in said receptacle, and a heater adapted to be maintained at a cracking temperature while in contact with said oil under pressure.

24. An apparatus of the nature disclosed, comprising in combination, a source of oil, a receptacle connected therewith, and a heater combined with said receptacle adapted to be maintained at a cracking temperature in contact with the oil therein, an outlet for the oily vapors evolved by the action of said heater, a receptacle connected with said outlet and adapted to collect portions of the oily liquid carried by said vapors, means for returning said collected liquid to the action of said heater, and means for condensing the residual vapors.

25. An apparatus of the nature disclosed comprising in combination, an oil tank, a receptacle connected therewith, an electric heater within said receptacle comprising a series of carbon rods, a plurality of carbon links connecting the adjacent ends of said carbon rods, and electrical connections extending from the exterior of said receptacle to the terminals of said electric heater.

26. An apparatus of the nature disclosed comprising in combination, an oil tank, a receptacle connected therewith, an electric heater within said receptacle comprising a series of resistance rods, a plurality of relatively infusible links connecting the adjacent ends of said resistance rods, electrical connections extending from the exterior of said receptacle to the terminals of said electric heater to enable a heavy electric current to pass through said rods to maintain the same at an elevated temperature while submerged in the oil contained in said receptacle, means for maintaining said oil at approximately a pre-determined level within said receptacle, and a pump for accelerating the relative movement between said electric heater and the oil contacting therewith.

27. An apparatus of the nature disclosed comprising in combination an oil tank, a receptacle connected therewith, a plurality of carbon tubes alternately connected by links and arranged in said receptacle to enable oil to flow through the bores thereof, means for supporting said tubes com- [fol. 1236] prising a heater located at a fixed point within said receptacle, means for maintaining oil within said receptacle to enable oil to constantly occupy and flow through the bores of said carbon tubes and means for heating said tubes.

28. An apparatus of the nature disclosed comprising in combination an oil tank, a receptacle connected therewith, an electric heater comprising a circumferentially arranged series of graphitic-carbon tubes, terminals supported by said receptacle and electrically connected with said heater and serving to maintain the same at a fixed position within said receptacle, electric connections extending from the exterior of said receptacle to the terminals of said electric heater, means for regulating the entry of oil to said receptacle whereby its level may be maintained at approximately a predetermined distance above said heater and means for heating said tubes.

In testimony whereof I affix my signature, in the presence of two witnesses.

Joseph H. Adams.

Witnesses: Leonard A. Watson, H. M. Seamans.

[fol. 1237] **PETITIONER'S EXHIBIT 186**

J. H. ADAMS.

PROCESS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

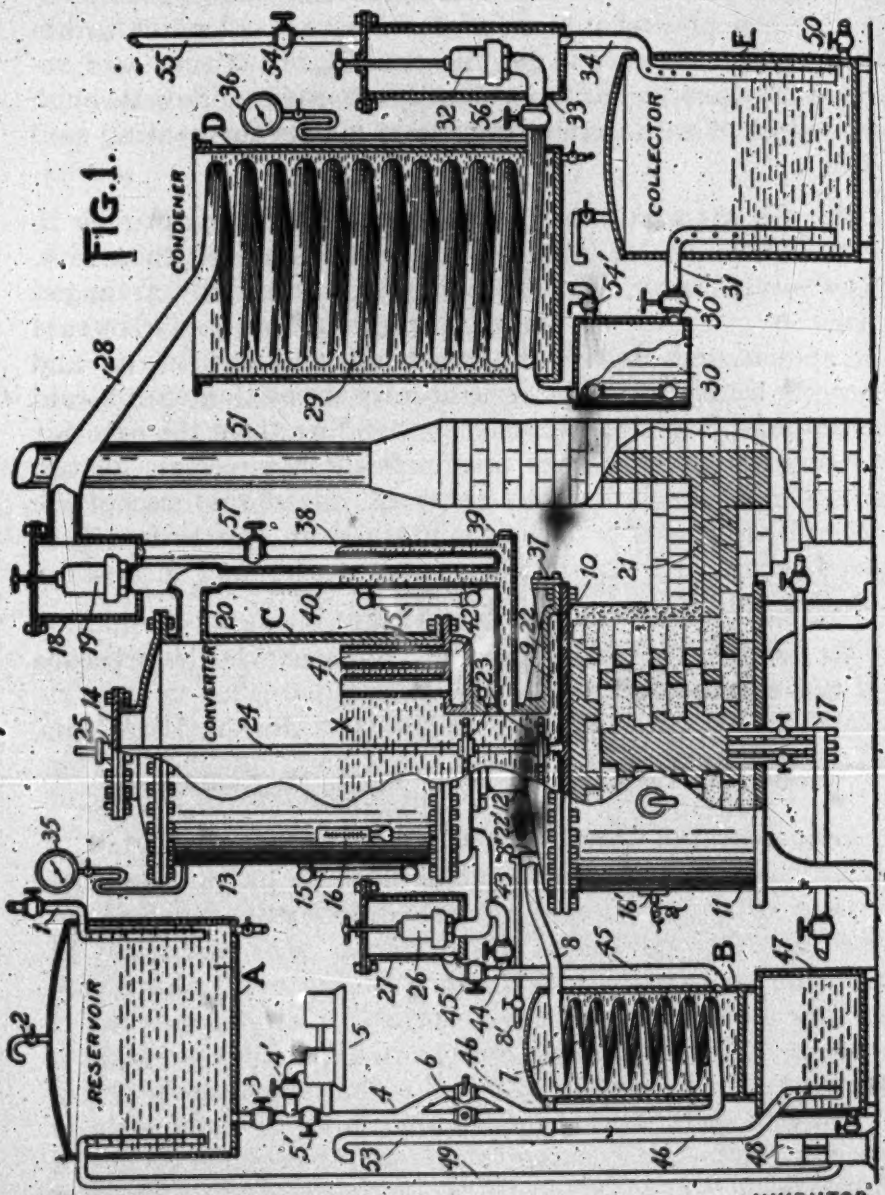
APPLICATION FILED DEC. 31, 1914.

1,320,726.

Patented Nov. 4, 1919.

2 SHEETS—SHEET 1

FIG. 1.



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PX 186-1

[fol. 1238]

J. H. ADAMS.

PROCESS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED DEC. 31, 1914.

1,320,726.

Patented Nov. 4, 1919.

2 SHEETS—SHEET 2.

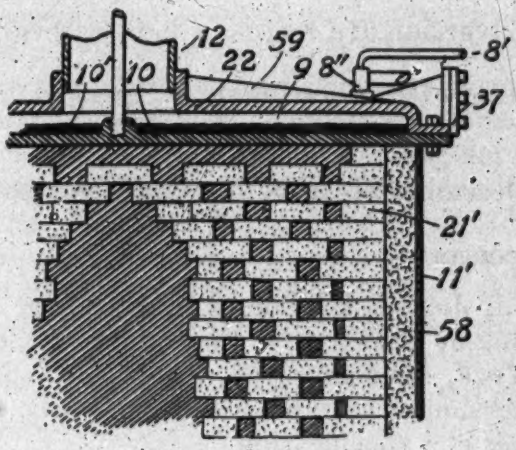

FIG. 2.

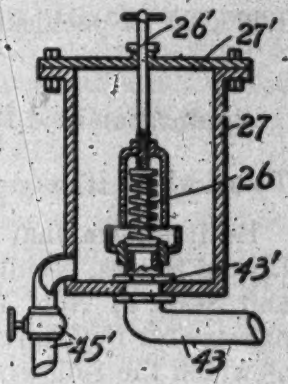

FIG. 3.

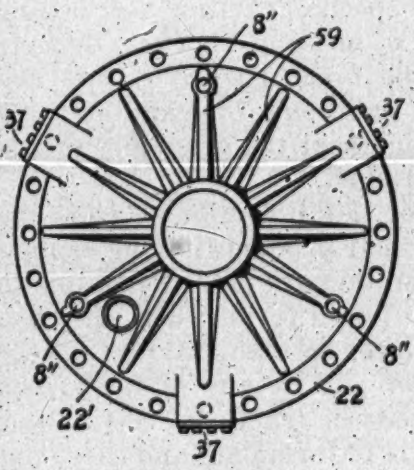

FIG. 4

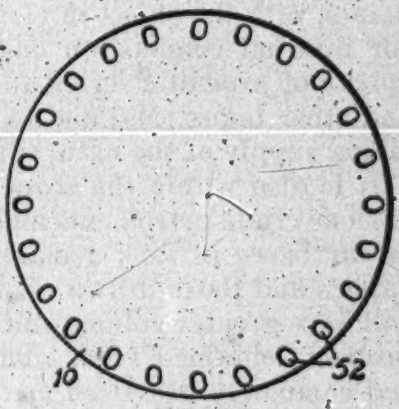

FIG. 5.

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PX186-2

INVENTOR.

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[fol. 1239] United States Patent Office

Joseph H. Adams, of Brooklyn, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Process for the Conversion of Liquids, Fluids, and Oils

1,320,726. Specification of Letters Patent. Patented Nov. 4, 1919

Application filed December 31, 1914. Serial No. 879,907

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented a new and useful process for the Conversion of Liquids, Fluids, and Oils, and of which the following is a specification.

My invention relates broadly to the art of converting oils and distillates of the plain hydro-carbon series, as well as those of the aromatic series, into more volatile products resembling light oils, gasolenes, benzines and naphthas which are characteristized by lower specfic gravities and boiling points, with the object in view of meeting the great demand for internal combustion engine fuels, gasolenes, oils and spirits of aromatic series and naphthas for manufacturing and other industries; and to augment the gradually diminishing supply of the natural product.

It is also within the scope of this invention to treat the various crude petroleums and their products having asphalt or tar bases in such a manner that the oils driven off in vapors and those drawn off in liquid form, when collected, will have greater volume and lower specific gravity than the products obtained from similar oils by any of the known and commonly practised methods of fractional distillation.

The object of this invention is to formulate and carry out in a continuous manner a process for bringing about the conversion and transformation of oil by means of externally applying a high degree of heat to a chamber, the whole or a part of which is composed of heat enduring material, and, while containing hydro-carbon or other oils, heating the walls of the chamber to a temperature of sufficient intensity

to locally "crack" and convert the said oil into oils and spirits essentially different from the original untreated oil.

This invention is based on the fact that petroleum oils and distillates can be successfully "cracked" and broken into those of lower specific gravities and boiling points by means of properly applied intense heat without unduly converting them into large quantities of fixed gases; and that these oils, when transformed by decomposition and synthetic reconstruction, form new chemical compounds, or products of a more valuable nature than the original untreated oils as set forth in my Patent 976,975, November 29, 1910, and pending applications of 417,714, 530,852 and 618,011.

By my process, however, it becomes quite feasible to convert a high specific gravity oil into those of lower specific gravities such as benzol, tuluol, benzin, naphtha and gasolene, by subjecting the oil or mixtures of oils to the powerful influence of properly applied external incandescent heat and decomposing temperature of not less than one thousand degrees, Fahrenheit (1000° F.), and from a visible cherry red in color to a full white heat, according to the character of the oil to be treated.

My object in general is to provide a new method and process for successfully breaking up the hydro-carbon oils as the low naphthas, kerosenes and fuel oils into those of greater commercial value comprising the lighter naphthas and gasolenes, benzols and tuluols to augment the natural supply now obtained by known methods of crude oil separation.

Broadly stated, my improved process, which is in contradistinction from mere fractional distillation methods, consists in subjecting hydro-carbon oil to a form of decomposition and reconstruction under the influence of intense heat and self-generated vapor pressure, whereby the product obtained, when condensed, collected and separated, will have greater commercial advantages than the original oil.

The nature of the process is such that its full disclosure may be greatly facilitated by describing certain characteristic features of an apparatus designed to carry out the same, and attention is directed to the accompanying drawings forming a part of this specification in which Figure 1 is an elevation and sectional drawing of the collective apparatus, and for all purposes of description this will afford a clear and well defined view.

Fig. 2 is a section at top of a furnace, which will serve to illustrate a common form of heater and the correlated parts of apparatus.

Fig. 3 shows more clearly a form of release valve and vapor or liquid collector.

Fig. 4 is a top plan of the crown which is mounted over [fol. 1240] the furnace or heater, and Fig. 5 is a plan of the hot plate or medium which, when heated to the proper incandescence brings about the conversion, as more fully set forth in the following description:—

In the drawings like characters of reference denote corresponding parts throughout the several views of which in Fig. 1, A represents a suitable supply apparatus or reservoir serving as a source for the oil to be treated.

This source of supply can be somewhat elevated with respect to the converter C, so that the gravity tendency of the oil may augment its flow into the converter under the influence of the contained weight of oil, or the ease with which it may be withdrawn and forced into the converter C by means of pump 5.

The fluid oil may be supplied to the container A through pipe 1, while at the same time the displaced air can escape through pipe 2, or this pipe may be connected with an air compressor which will maintain a sufficient pressure over the surface of the oil to force it through discharge valve 3, pipe 4 and through the regulating feed valve 6, to the pre-heater B, of which 7 represents a pipe coil through which the oil flows and is heated before entering the cracking chamber 9, of converter C, through pipe 8.

For obvious reasons, it is best to pre-heat the oil before it is admitted to the converter C, so that the heat in that part of the apparatus may be conserved for the more important function of "cracking", splitting the molecules of and rapidly vaporizing the converted oils; and therefore the heater B, is provided wherein the oil to be treated may be brought to any desired temperature within the coils 7, by any economical means of heating.

This oil heater B, is placed in the piping system between the source of oil supply A, and the converter C, in a manner conducive to the best methods of admitting oil to the cracking chamber of the converter C.

The drawing shows one of the many diverse forms which the converter C may assume, and such converter here shown

comprises a chamber 9 of oil containing capacity having a heat enduring bottom plate 10, located directly over a heating medium or furnace 11.

The chamber 9, is connected by a pipe or neck 12 directly with an inclosed expansion dome 13, intended to contain both liquid and vapor, and closed at the top by means of cap 14.

A gage glass 15 and thermometer 16 can be arranged on the vapor and liquid dome 13, for the inspection of oil quantities and temperatures, which are regulated by the flow of oil through supply pipe 4, and controller valves 6.

A gage glass 15′ is arranged on column 40 also, in order to inspect the location of oil in that part of the system.

The furnace 11 is provided and located under the liquid containing parts of converter C, as a means of generating intense heat by known methods of gas, fuel oil, coal or electricity, and this furnace is supported on legs or piers, if necessary, so that in the use of gas or fuel oil, the piping system, valves and controllers 17 can be the more readily operated.

A pyrometer element 16′ is arranged to extend through the walls of the furnace in order that temperature may be determined, which, in this process is a very important feature.

Inasmuch as the vapor rising into and filling the upper part of the expansion dome 13 may, at any time, be so rapidly evolved as to exert undue pressure; I have placed a collecting tank 18 and pop valve 19, in relation with the upper part of dome 13, by means of the pipe 20, so that any sudden pressure above a given number of pounds necessary to carry on the process under normal conditions, will cause the pop valve 19 to act rapidly and relieve the excessive pressure.

A feature of primary importance is the means for externally applying heat of intense temperature to the heat enduring plate 10, for the purpose of bringing about a more or less complete conversion of oil.

Preferably this feature is operated by gas or fuel oil and air or steam under pressure, and comprises one or more jets 17, through which elements of combusion are forced into an inclosed furnace or retort 11, composed of a shell or container 11′, as shown in Fig. 2, lined with firebrick 21′ and asbestos or magnesia filling 58, which together are intended to retain the heat as long as possible, for the purpose of

maintaining the plate 10 at the proper and uniform temperature.

In the shown form this furnace 1, with its intake pipes 17, and outlet or exhaust flue 21, passing through stack 51, is made up in circular form to properly heat the round plate 10, located at its top in the form of a cap; and while the design of heater may be varied to conform to the different shapes and styles of converters, this form is well adapted for the economical use of gas and liquid fuels supplied under pressure to generate the required intense heat; especially for working in the oil and gas regions where the fuel cost is low.

The intense externally applied heat affects the oil contained within the cracking chamber 9 in such a manner as to very effectually convert the same and is thus adapted to assist in a step of primary importance to my process.

[fol. 1241] I may here state that when operating upon certain oils it is desirable to localize the application of heat so as to prevent the spread of the heat in a lower degree of intensity than is necessary to efficiently "crack" the oil, but of a sufficient intensity to cause evaporation of undue amounts of oil at a distance from the intensely heated walls of the cracking plate 10, without bringing about the desired conversion.

To this end in the embodiment of the apparatus shown in Fig. 1, I have provided a crown plate 23, to which the "cracking" plate 10 is made fast with bolts drawn against a gasket at its outer edge, and spaced them so that only a thin layer of oil comes in close proximity to the intensely heated surface of the plate 10 which, as shown at Fig. 5, is provided with slotted holes 52, having parallel edges radiating from the center of the plate, so that as expansion or contraction takes place in the plate, a means is provided to prevent upsetting the anchorage bolts or breaking the cracking chamber crown 22.

A more comprehensive idea of this crown can be had by referring to the drawing, Fig. 4, where in three ports 37, and three oil supply pipes 8″ are definitely located to facilitate operation. This drawing also shows the series of ribs 59 radiating from the center, and which lend strength to this part of the apparatus.

The sight tube 22′ provides a means of inspecting the incandescence of the cracking plate 10, or the molten metal

10′ (Fig. 2) while the converter is in operation; and also affords a port through which pieces of metal or alloy can be placed in the chamber 9, preparatory to its being melted.

To protect the plate 10 from burning out, or the destruction of the oil over its surface and its complete transformation into fixed gases, with a consequent heavy and clogging deposit of carbon, I employ a metal or alloy having a melting point consistent with the required "cracking" temperature for the oil to be treated; which, when brought to the proper degree of heat, becomes a fluid metal 10′ (Fig. 2) flowing over the top surface of the plate 10, where it can be seen through inspection sight 22′, and remaining so during the process of oil conversion while the furnace heat is maintained at the proper degree of intensity.

In this manner the oil does not come in direct contact with the heated plate 10, but is affected by indirect heat absorbed through the molten metal, and which treats it as required but without the undesirable accumulation of carbon which is destructive to the heat enduring plate 10.

Alternately, and for the treatment of certain oils, the molten metal or alloy can be omitted from the apparatus, when in operation, so that the oil may come in direct contact with the intensive heated surface of plate 10; and the choice between these two methods of oil contact is largely a matter of judicious oil practice over which no set rules can govern.

In order to prevent furious agitation within the chamber 9, and dome 13, while the process is in operation, perforated baffle plates 23, are located on the rod 24, and made fast so that they occupy a position within the connecting neck or pipe 12, and are held in place by means of a nut and gland 25, at the top of dome 13, through which it passes.

Owing to the excessive quantity of heat employed in this process, and the consequent volatilization of unconverted oils under ordinary atmospheric conditions, I have, by a series of valves and collecting tanks, provided a means of carrying on the conversion process under a pressure of several atmospheres, if necessary, by setting the pop valves to operate at certain pressures, as may be indicated by gages 35 and 36, both for the release of vaporized oil from the top of dome 13 through pop valve 19 and chamber 18, and liquid oil from the bottom of said dome through pop valve 26 and collecting tank 27.

In this manner I am able to reduce the undesirable vaporization without conversion to a minimum, and as a conse-

quence the evolved oils are, in a large proportion "cracked" and otherwise converted in character.

In addition to the intense heat employed for the purpose of conversion, I also may use superheated steam forced into the body of oil through pipe 8′ and a small jet at its point of entry 8″ into the chamber 9, and regulate the supply of steam in proportion to the amount of oxygen required to combine with a certain quantity of carbon contained in the oil, and thus freeing the resultant vapors, the product of conversion, from a portion of undesirable carbon.

In Fig. 3, a detailed drawing shows a form of liquid or vapor trap, wherein 27 is the container or expansion tank, provided with a tightly fitted cover 27′ held on with bolts and a gasket at its outer edge.

The pop valve 26 is arranged centrally on an elbow of pipe 43, and made fast to the container with flanges or lock nuts 43′.

The pop valve can be regulated for various pressures by means of the rod and cross head 26′, which projects through the cap 27′ and is properly sealed by a stuffing box or gland.

Oil or vapor escaping through the pop valve 26, and collected within the chamber 27, is then discharged through pipe and valve 45′ to its destination.

By the proper means of propulsion, the oil will be con- [fol. 1242] stantly flowing toward and into contact with the intensely heated lower surfaces of the cracking chamber 9, to take the place of that already vaporized from above, or that drawn from below the surface line of oil maintained in the dome C, as indicated by the dotted line X.

Newly admitted oil will in turn be "cracked" and changed in the apparatus into lighter and more volatile products, which will pass off in the form of vapors through the tank 18 and gooseneck 28, into the pipe coils 29 of condensing apparatus D; and having been condensed in the usual manner the condensate is discharged into collecting tank E, through trap tank 30, valve 30′ and pipe 31; or through pop valve 32 and tank 33, then conducted through pipe 34, according to the method to be employed for operation with the apparatus under partial or complete compression.

During the operation of the process for oil conversion by this method, the raw non-converted oils will be relieved of a certain portion of free carbon, of which they are in

part composed, as well as some of the foreign substances which it is desirable to eliminate.

This, of course, alters their chemical character and converts them from one or more of the hydro-carbon series into others of an essentially different character.

The carbon and other sediment remaining on the top surface of plate 10, or the molten metal 10′ above it, can be removed from time to time by cooling down the furnace, withdrawing the oil, and opening the ports 37 in the cap 22; which are more clearly shown in Figs. 2, and 4, and with a narrow scraper or long slicing chisel, the refuse may be removed.

Inasmuch as the precise degree of temperature at which the plate 10, should be maintained in practice, will largely depend upon, and be varied with particular conditions, it will be sufficient to state that the temperature of the plate will generally vary from a cherry red to a full white heat, according to the nature of the oil to be treated, and that at no time in the process of conversion will the plate 10 be below a temperature of one thousand degrees Fahrenheit, (1000° F.).

When operating, it has been observed that apparently only a certain part of the fluid vaporized comes in direct contact with the intensely heated surface of the "cracking" plate 10, for the reason that the intensity of heat evaporates a certain portion of the oil at a lower temperature than is required for "cracking" the oil.

Accordingly, the vapors passing into the dome will be composed not only of the oil which has been transformed; but will also contain a certain portion of the unchanged original oil in the form of vapors which, when condensed and collected, must be separated by one of the processes of fractional distillation, if a more or less perfect segregation is required.

Since some of the vaporized original and unconverted oil may tend to condense in the tank 18, after leaving the pop valve 19, and before reaching the gooseneck 28; a pipe 38 is connected to the bottom of tank 18, and leads back through pipe 39, into the neck 12, of the converter C.

In a like manner if vapors containing heavy molecules or spray of unconverted oil, rise to the top of dome 13, and pass out through pipe 20, and condense before passing through valve 19, the condensate is led down through column 40, and into neck pipe 12, through pipe 39.

In this manner the already condensed unconverted oil may be passed into the system again to mingle, and possibly become converted, with the new supply of oil continually flowing into the cracking chamber 9.

The above specifically described apparatus may, of course, be modified greatly and yet be well adapted to carry out one or more of the essential correlated steps of my process which, having now described a form of apparatus, is carried on in the following manner:

When operating under atmospheric conditions, and without pressure in the systems, oil is admitted to container A through pipe 1, the displaced air in the container passing out through pipe 2, until a sufficient amount of oil is stored for progressive work.

The system is then supplied with oil from the container through valve 3, and pipe 4, passing pump 5, which is cut out by closing valve 4', thereby allowing the oil to pass through valve 5' and precision valves 6, into the coils 7 of pre-heater B.

The oil circulating through these coils, where it is heated, is then passed through pipe 8, into cracking chamber 9, of the converter C, where it is brought into contact with intense heat maintained in plate 10.

The oil is held at a uniform level in dome 13, as indicated by the dotted line X, for the purpose of supplying weight to hold the body of oil down against cracking plate 10, or molten metal 10', and also to provide a medium for the partial arrest of up-flowing converted vapors, which are rapidly evolved by the treatment of oil subjected to intensely high temperature.

As the vapors rise through pipe neck 12, to escape into the upper part of liquid and vapor dome 13, an intense agitation is carried on within this pipe 12, which would cause undue disturbance over the surface of the oil at line X; therefore perforated baffle plates 23, are made fast to rod 24, which is attached to the top 14, of the dome 13, [fol. 1243] by means of a nut and gland 25 and the lower end screwed into cracking plate 10, where it is held securely in place.

As the oil rapidly becomes heated and volatilized, and would expand to unreasonable bounds if confined in the dome for any length of time, the overflow pipes 41, are provided to carry off the surplus unconverted oil which flows

down through them into collecting chamber 42 and out through pipe 43 and valve 44, to pipe 45, through which it is admitted to the bottom of preheater B, and flows out of the top through pipe 46, to the overflow tank 47, from which it is withdrawn by pump 48, and delivered through pipe 49, to container A.

This returned oil may then be supplied again to the converter through the system just described.

A certain small portion of oil having been "cracked," converted and vaporized, rises to the top of dome 13 and passes out through pipe 20, pop valve 19, in container 18, which is opened and made a free passage to gooseneck pipe 28.

It then passes through condensing coils 29, immersed in water contained in tank D, and flows through trap tank 30, valve 30', and pipe 31, into collecting tank E, from which the condensate may be drawn off through valve 50.

An important feature of pre-heater B, is the vent pipe 53, at the upper end of pipe 46, through which air and gases may pass to avoid vacuum or pressure within the container B, and which would interrupt the proper flow of hot oil through that apparatus.

When operating under complete pressure brought about by the expansion, vaporization and partial retention of oil and vapors in dome 13, due to the applied heat to plate 10, as in a steam boiler, valve 5' in pipe 4 is closed. Valve 44 in pipe 43 is also closed, as well as valve 30' in pipe 31.

The pop valve 26 in container 27, is set to the proper release pressure, also pop valve 19 in container 18, and 32 in container 33.

The valve 56, at the end of coil 29, is open, while the valve 57, in pipe 38 is closed; thus effectually sealing the system against operation under atmospheric pressure.

Oil is then withdrawn from container A, through valves 3 and 4', by pump 5, which forces it through pipe 4 and valves 6, to the pre-heater coils 7, and pipe 8, into the cracking chamber 9.

A certain portion of unconverted oil overflows from the surface level X, in the dome 13, and is conducted through pipes 41 to chamber 42, thence through pipe 43, to pop valve 26, in container 27, where, by the self generated vapor pressure maintained over the surface of oil in the dome 13, the pop valve 26 in tank 27, is caused to release and allow

a portion of the oil to flow through pipe 45, into the lower part of pre-heater B, and escape from the upper part of said container through pipe 46, to the overflow tank 47.

The residue oil may then be returned to tank A, as heretofore described.

That certain portion of oil which, having come in contact with the hot plate 10, or molten metal 10′ lying above it, and becomes vaporized; rises through neck 12, and body of oil contained in the lower part of dome 13, and expanding into the upper part of the said dome, is driven off through pipe 20, pop valve 19, and into the condensing coils 29, through pipe 28.

Pop valve 32, in container 33, is set at a pressure sufficient to check the rapid flow of condensate from the coil, and is therefore an adjunct in maintaining vapor pressure within the entire system from pump 5 to the release valve 32. Distillate can also be accumulated under vapor pressure, in trap tank 30, then released through valve 30′ and pipe 31. The oil, having passed the last checking point, then flows by gravity into the collecting tank E.

If a partial pressure only, is required in the system, the valve 56 and pop valve 32, also valve 30′ in pipe 31 are opened, thus giving a free run of vapor and condensate, at atmospheric pressure only, from the container 18, to the collecting tank E, at the foot of the pipe train.

Gases which may be present in the distillate, or fixed gases made in the process of conversion, can escape through valve 54 and pipe 55, leading out from container 33, or through valve 54′ leading out from trap tank 30.

As the condensate collected in tank E, is of a complex nature composed of converted and un-converted original oil, it may be withdrawn and separated by any of the methods of fractional distillation and the remainder returned to container A, for retreatment as before.

From the foregoing disclosures it is apparent that I have succeeded in formulating a process well suited to the several objects in view, and that as a result I have made it possible, within commercial limits, to convert inexpensive available oils into products of greater value.

In view of these disclosures, it is obvious to those skilled in the art, that my process may be carried out with different fluids by varied steps, and accordingly I intend that all matter contained in this description shall be taken as illustrative and not in a limited sense.

I desire it to be understood also, that the language [fol. 1244] adopted in the following claims is intended to cover all of the generic and specific features of this invention, and all statements of the scope thereof which, as a matter of language, might be said to fall therebetween.

The apparatus described in the foregoing specification is not claimed herein, but forms the subject matter of a process for accomplishing the required results, and, having now described my invention, what I claim as new, and desire to secure by Letters Patent is:

1. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil under vapor pressure, maintaining a portion of said oil relatively separate and distinct, subjecting said separate portion of said oil to a cracking and converting temperature, and introducing superheated steam into the portion of said oil where said cracking temperature is applied.

2. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil in an inclosed chamber, maintaining a portion of said oil relatively separate and distinct, subjecting said separate portion of oil to a cracking and converting temperature, maintaining superatmospheric vapor pressure on said body of oil, and introducing superheated steam into said body of oil.

3. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil is an inclosed chamber, maintaining a portion of said oil relatively separate and distinct, subjecting said separate portion of oil to a cracking and converting temperature, introducing superheated steam into said oil where said cracking temperature is applied, condensing the converted vapor products generated and maintaining self-generated vapor pressure on said oil undergoing treatment and on said vapors while being condensed.

4. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil under vapor pressure, maintaining a portion of said oil relatively separate

and distinct, subjecting said separate portion of said oil to a cracking and converting temperature, continuously introducing oil and superheated steam into said body of oil at the point where said cracking temperature is applied and continuously conducting away and condensing the vapors generated.

5. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil in an inclosed chamber, maintaining a portion of said oil relatively separate and distinct, subjecting said separate portion of oil to a cracking and converting temperature, continuously introducing oil and superheated steam into said body of oil at the point where said cracking temperature is applied, continuously conducting away and condensing the vapors generated and maintaining vapor pressure on said confined body of oil and on said vapors undergoing condensation.

6. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil within inclosed containers, subjecting a portion of said oil below the surface to a local cracking and converting temperature, continuously introducing oil into said body at the point where it is subjected to the local cracking temperature at a rate greater than that at which the oil is converted, withdrawing oil from the upper portion of said body at such a rate as to maintain a substantially constant volume and level of oil and condensing the converted products.

7. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil, subjecting a portion of said oil below the surface to a local cracking and converting temperature in excess of their volatilizing points, continuously introducing oil into said body at the point where it is subjected to the local cracking temperature at a rate greater than that at which the oil is converted, withdrawing oil from the upper portion of said body at such a rate as to maintain a substantially constant volume and level of oil, condensing the converted products, and maintaining self generated vapor pressure on said body of oil and on said vapors during condensation.

8. The herein disclosed process of converting high boiling point hydrocarbons into lower boiling point products which consists in confining a body of oil, subjecting a portion of said oil below the surface to a local cracking and converting temperature, continuously introducing preheated oil and superheated steam into said body of oil below the surface, withdrawing oil from the upper portion of said body at such a rate as to maintain a substantially constant volume and level of oil, condensing the vapors of converted oil in free communication with said body of oil and maintaining self generated vapor pressure on said oil during conversion and on said vapors during condensation.

9. The herein disclosed process of converting oils which consists in confining a body of oil of considerable volume, subjecting a limited portion of said oil at the lower part [fol. 1245] of the body to a local cracking temperature, continuously supplying preheated oil and superheated steam to said limited portion subjected to said cracking temperature, drawing off oil from the upper portion of said body to maintain a substantially constant volume of oil and condensing the vapors of the converted oil.

10. The herein disclosed process of converting oils which consists in confining a body of oil of considerable volume, subjecting a limited portion of said oil at the lower part of the body to a local cracking temperature, continuously supplying preheated oil and superheated steam to said limited portion subjected to said cracking temperature, drawing off oil from the upper portion of said body to maintain a substantially constant volume of oil, drawing off the converted vapors under pressure from above said oil and condensing them under pressure.

11. The herein disclosed process consisting in subjecting high boiling point hydrocarbons to an externally applied heat of intense temperature while contained in a heat enduring chamber, maintaining a self generated vapor pressure only in the chamber and to and through the condenser in free communication with said chamber, introducing superheated steam under high pressure into the body of oil undergoing transformation, locally cracking

and converting the same into low boiling products essentially different from the original untreated oil, separating out the lighter and retreating the heavier residues.

In testimony whereof I affix my signature in the presence of two witnesses.

Joseph H. Adams.

Witnesses: Joel S. de Selding, A. Capstick.

[fol. 1246]

PETITIONER'S EXHIBIT 187

J. H. ADAMS.

APPARATUS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED MAR. 29, 1915.

1,320,727. Patented Nov. 4, 1919.

2 SHEETS—SHEET 1.

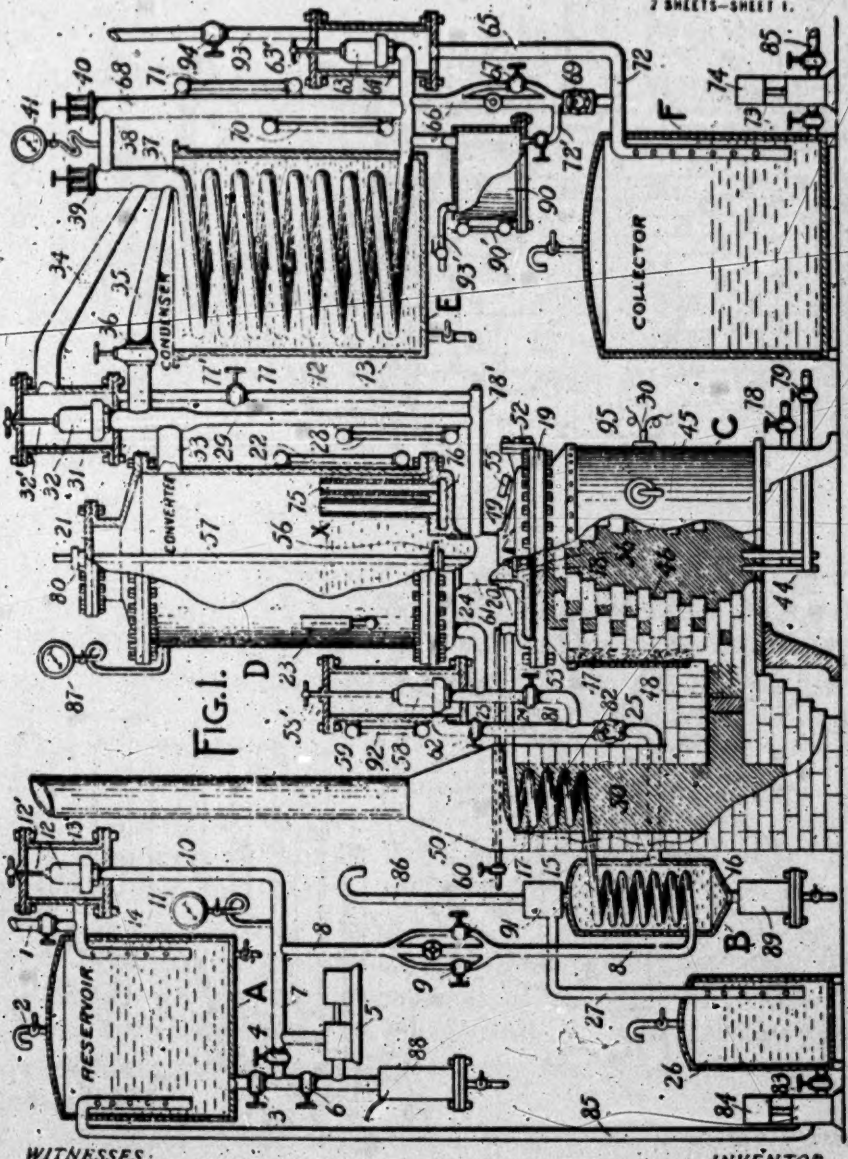

FIG. 1.

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PX187-1

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APPARATUS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED MAR. 29, 1919.

1,320,727. Patented Nov. 4, 1919.

2 SHEETS—SHEET 2

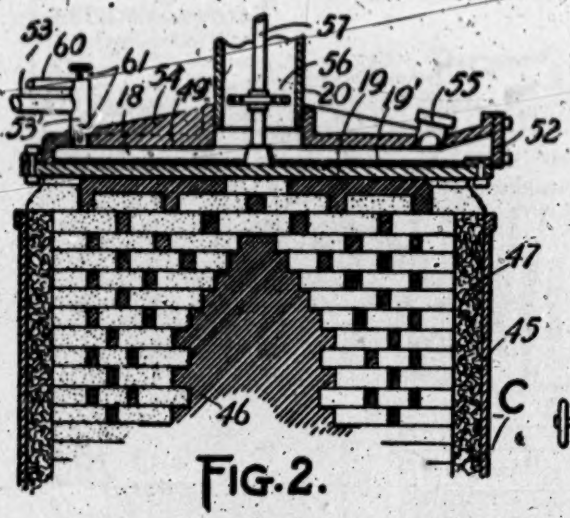

FIG. 2.

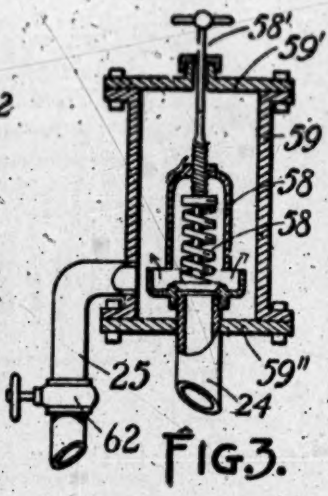

FIG. 3.

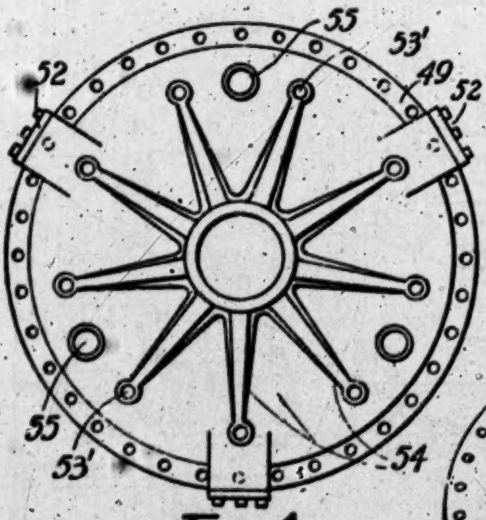

FIG. 4.

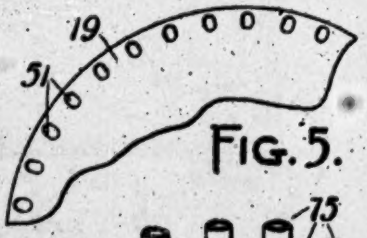

FIG. 5.

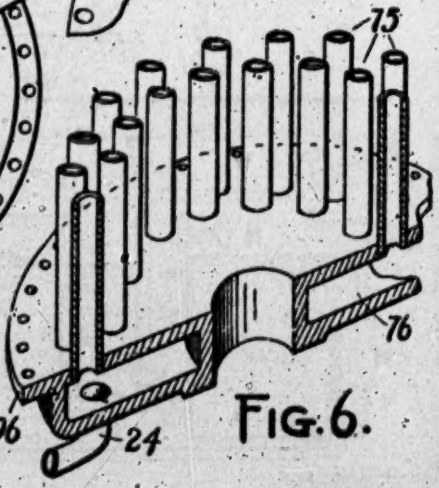

FIG. 6.

WITNESSES

A Capatick

Joel B. DeBelding

P.X.187-2

INVENTOR.

Joseph H. Adams

[fol. 1248] United States Patent Office

Joseph H. Adams, of Flatbush, New York, Assignor to The Texas Company, of Houston, Texas, a Corporation of Texas

Apparatus for the Conversion of Liquids, Fluids, and Oils

1,320,727. Specification of Letters Patent. Patented Nov. 4, 1919

Application filed March 29, 1915. Serial No. 17,699

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Flatbush, in the county of Kings and State of New York, have invented a new and useful Apparatus for the Conversion of Liquids, Fluids, and Oils, of which the following is a specification.

Description

My invention relates broadly and primarily to an apparatus for converting high boiling point petroleum oils and distillates as well as those of the aromatic series into more volatile products resembling lower boiling oils of the gasolene, benzin, naphtha type and larger yields of benzol and other low specific gravity products of the aromatic group to augment the gradually diminishing supply of the natural product, or that which is presently obtained from crude petroleum and coal tar by the commonly practised methods of fractional distillation, in order to meet the increasing demand for these products.

It is intended that this conversion apparatus shall be available for the transformation of oils and oily vapors of the hydrocarbon series and for all other conversion and reactionary methods and practices for which it may be adapted.

One object of this invention is to provide a suitable apparatus in which to carry out, in a continuous manner, a process for bringing about the conversion and transformation of oils and oily vapors by means of externally applying a high degree of heat to a chamber, the whole or part

of which is composed of heat enduring material, and while containing hydro-carbon oils or oily vapors under vapor pressure, heating the walls of the chamber to a temperature of sufficient intensity to crack and convert the same into oils or petroleum and coal tar oils and spirits different and possibly more valuable than the original untreated oil.

This invention is based on the facts that hydro-carbon oils and vapors of oil distillates can be successfully and commercially converted into those of lower specific gravity and boiling points, by means of properly applied intense heat and high vapor pressure, without unduly transforming them into a large quantity of fixed gases as more fully set forth in my co-pending applications 530,852, December 1, 1909, 618,011, March 30, 1911, and 879,907, December 31, 1914. The products produced by the transformation differ in character from the original material and for certain purposes are more useful and more valuable.

This invention comprises an apparatus capable of being constructed at a moderate cost, and so designed as to enable skilled workmen to readily operate the same at a high rate of efficiency in lowering the boiling points of various grades of hydro-carbon oils.

Another object within the contemplation of this invention is to provide an apparatus capable of some variation in the mode of operation, so as to adapt the same to the treatment of different oils, where simple and inexpensive parts and features can be arranged and correlated to render complete an organization or system of continuously converting hydro-carbon oils and oily vapors on a common basis, in an apparatus of practical and enduring nature, where in the more valuable materials such as naphthas, gasolenes, benzols and toluols of low specific gravities can be converted from oils of less value and higher boiling points.

Other objects and advantages of my invention will be set forth hereinafter, and the novel features thereof set forth in appended claims.

In order that this invention may be the more fully disclosed and otherwise made wholly comprehensible to those skilled in the art, drawings typical of the many possible embodiments thereof have been appended hereto, as a part of this disclosure, and in such drawings like characters of

reference denote corresponding parts throughout the several views of which:

Figure 1, is an elevation and partly sectional drawing of the collective apparatus embodying certain aspects of this invention wherein heat of intense temperature is applied to oil and oily vapors while under vapor pressure, and also showing details of the various parts, and which, for all purposes of description, will afford a clear and well defined view of the several features comprising the converting apparatus and its correlated pumps, tanks and containers.

Fig. 2 is a sectional view at the top of a furnace, shown [fol. 1249] to illustrate a common form of heater which may be adapted for this work, and also the correlated local parts of the heating and oil or oily vapor cracking apparatus.

Fig. 3 shows more clearly a form of release pop valve and oil vapor and liquid collector.

Fig. 4 is a top view of the cracking chamber crown, to the under side of which the cracking plate is attached, and which is mounted over the furnace or heater.

Fig. 5 is a partial or segmental plan of the cracking plate or medium which, when brought to the proper and required intense heat by means of the underlying furnace, brings about the desired conversion, as more fully set forth in the following description, and:

Fig. 6 is a partly sectional view of the liquid and vapor dome base showing the circular rows of overflow pipes, liquid receptacle and discharge pipe.

The Reservoir Tank, A

Referring now to Fig. 1, the source of supply A, can be somewhat elevated with respect to the converter C—D, so that the gravitating tendency of the oil may augment its flow into the converter under the influence of contained weight of oil, or the ease with which it may be withdrawn and forced into the converter by means of pump 5.

The fluid oil may be supplied to the container A, through the pipe 1, while at the same time displaced air from the tank can escape through vent pipe 2, at the top of the container.

For obvious reasons it is best to pre-heat the oil before it is admitted to the converter C—D, so that the heat in that part of the apparatus may be conserved for the more important function of "cracking," splitting the molecules of, and rapidly vaporizing the converted oil, and therefore the heating system B, is provided and interposed between the source of supply and the converter, wherein the oil to be treated can be brought to any desired temperature.

This pre-heater may be of any suitable type, but preferably provides a continuously rising coil 15, contained within the hot oil receptacle 16, where the overflow hot oil from the dome D, supplied through pipes 24 and 25, can be utilized to heat the incoming cold oil within the coil, or the pipe coil 17, located in stack 50, can be arranged to utilize the waste heat from the furnace C, to pre-heat the inflowing hot oil to the converter C—D.

The oil to be so heated is preferably admitted to the bottom of the coils and progresses upwardly in its flow, so that any bubbles or vapor may rise and readily escape and not form air locks to retard the flow or oil into the converter.

The Oil Converting Receptacle, C—D

The drawing shows one of the many diverse forms which the converter C—D, may assume, and such converter here shown comprises a cracking chamber 18, of oil containing capacity, having a crown 49, and a heat enduring bottom plate 19, located directly over a heating medium or furnace C.

The chamber 18, is connected by a pipe or neck 20, directly with an inclosed expansion dome D, intended to contain both liquid and vapor, and closed at the top by means of a cap 21.

A gage glass 22, and thermometer 23, can be arranged on dome D, for the inspection of oil quantities and temperatures, which are in part regulated by the flow of oil through supply pipe 8, and precision valves 9, and in part by the overflow of oil through pipes 24 and 25, pre-heater tank 16, pipe 27, and into hot oil receiving tank 26.

A glass gage 28 is arranged on column 29, in order to inspect the location of oil in that part of the system.

The furnace C, is provided and located under the liquid and vapor dome D, and cracking chamber 18, as a means

of generating intense heat by known methods of gas, fuel oil, coal or electricity; and this furnace is supported on legs or piers, if necessary, so that in the use of gas or fuel oil, access can be more readily had to the feed valves and controllers which may be located in the underlying pipe system.

A pyrometer element 30, is arranged to extend through the walls of the furnace C, in order that temperatures may be determined therein, which, in this conversion system, is a very important feature. A port 95, is located in the furnace wall, for inspection purposes, which same is closed with a suitable fire brick plug, provided with a handle.

Inasmuch as the vapors rising into and filling the upper part of the expansion dome D, may, at any time, be so rapidly evolved as to exert undue or spasmodic pressure, I have placed a collecting trap tank 31, and release pop valve 32, in close relation with the upper part of the dome, by means of the pipes 33 and 29, so that any undue or sudden pressure above a given number of pounds necessary to carry on the process work under normal conditions, will cause the release pop — 32, to act rapidly and relieve the excessive pressure into goose neck pipe 34, condenser head 37, and the coils 42, of apparatus E. A feature of primary importance is the means for externally applying heat of intense temperatures to the heat enduring or cracking plate 19, for the purpose of bringing about a more or less com- [fol. 1250] plete conversion of oil.

Preferably this feature is operated by gas or fuel oil, and comprises one or more jets 44, to which elements of combustion are fed through pipes 78 and 79, and thereafter forced into an inclosed furnace C, composed preferably of a metal shell, or container 45, lined with fire brick 46, and asbestos or magnesia filling 47, which together are intended to retain the heat as long as possible, for the purpose of maintaining the plate 19, at the proper and uniform temperature for more or less perfect conversion.

In the show form, this furnace C, with its intake pipes 44, and outlet or exhaust flue 48, passing through stack 50, is made up in circular form, and partially filled with a checker work of fire brick 46, to properly heat the round plate 19, located at the top of the furnace in the form of a cap; and while the design of heater may be varied to conform with the different styles of converters which could

be made, this form is well adapted for the economical use of gas and liquid fuels, to generate the required intense heat, and especially for operating in the oil and gas regions, where the fuel cost is low.

When operating on oils for the purpose of converting them, it is necessary to localize the heat so as to prevent its spreading in a lower degree of intensity than is necessary to effectually "crack" the oil, and to this end, in the embodiment of the apparatus, I have provided a crown 49, to which the cracking plate 19, is made fast with bolts drawn against a gasket at its outer edge and spaced them so that only a thin layer or body of oil contained in the chamber 18, comes in close proximity to the intensely heated surface of the plate 19, which, as shown at Fig. 5, is provided with slotted holes 51, having parallel edges radiating from the center of the plate, so that as expansion or contraction takes place in the palte 19, a means is provided to protect the crown 49.

A more comprehensive idea of this crown can be had from Fig. 4, wherein three ports 52, and a number of oil supply pipes 53', are definitely located to facilitate operation.

This drawing shows the radiating ribs 54, which help to strengthen that part of the apparatus.

The sight tubes 55, provide a means of inspecting the condition of the cracking plate 19, or the molten metal 19', (Fig. 2) while the converter is in operation; and also affords a port through which pieces of metal or alloy can be placed within chamber 18, preparatory to its becoming melted on plate 19.

To protect plate 19, from burning out, or the destruction of oil over its surface, with a consequent deposit of carbon and the more of less complete transformation of oil into fixed gases, with large commercial losses, I employ a metal or alloy having a melting point consistent with the required "cracking" temperature for the oils to be treated; which, when brought to the proper degree of heat becomes a semifluid metal 19', (Fig. 2) flowing over the top surface of the plate 19, where it may be seen through inspection sights 55, if there is clear oil in cracking chamber 18, and remaining so during the process of conversion, when the furnace heat is maintained at the proper degree of intensity.

In this manner the oil does not come in direct contact with the plate 19, but is affected by the molten metal which protects the upper surface of the cracking plate from the undesirable and destructive accumulation of carbon resulting from the process of "cracking."

Alternately, and for the treatment of very light gravity oils, the molten metal can be omitted from the apparatus, when in operation, so that the oil may come in direct contact with the intensely heated surface of plate 19, and the choice between these two methods of oil contact with the heat is largely a matter of judicious oil converting practice over which no set rules can govern.

In order to prevent furious agitation within chamber 18, and dome D, while the converter is in operation, baffle plates 56, are located with the neck pipe 20, and made fast to rod 57, which rod extends through cap 21, of dome D, and to which it is attached by means of lock nuts, then the joint is properly sealed with a gland or stuffing box 80.

The baffle plates located in this manner will overcome any undue geyser action or oscillation of the oil while being subjected to the intense heat within chamber 18.

Owing to the high temperatures employed in the conversion process, and the consequent volatilization of unconverted oils treated under ordinary atmospheric conditions, I have, by a series of valves and collecting trap tanks, provided means for carrying on this process under vapor pressure of several atmospheres, if found necessary, by setting release pop valves to operate at certain pressures, as indicated by gages 41 and 87, both for the release of vaporized oil from the top of dome D, through valve 32 and tank 31, and liquid oil from the bottom of dome D, through pipe 24, valve 58, in tank 59, from which it flows through pipe 25, and valve 62, and is collected in hot oil tank 26.

In this manner I am able to reduce the undesirable vaporization, without conversion, to a minimum, and as a consequence the oils and oily vapors are, in a large proportion, "cracked" and otherwise converted in character without, however, transforming them into the undesirable [fol. 1251] olefins and ethylenes, which are offensive in odor and uneconomical for commercial purposes.

In addition to the intense heat and high vapor pressure employed for the purpose of conversion, I also may use superheated steam forced into the body of oil or oily va-

pors through pipe 60, and small jets or nozzles 61, and which are provided to inject steam with the oil at its point of entry into the cracking chamber 18.

A valve regulates the supply of steam in proportion to the amount of oxygen required to combine with a certain portion of carbon contained in the oil and which is cracked out ordinarily by the intense heat, and also to add hydrogen to the oil or oily vapors to assist in lowering the boiling point and increase the yield of converted products.

In this manner the product of conversion is freed from a portion of undesirable carbon, which would otherwise accumulate in the cracking chamber and in time retard the progress of oil transformation.

During the operation of the process, the raw non-converted oils will be relieved of a certain portion of free carbon, of which they may be in part composed as well as some of the foreign substances which it may be desirable to eliminate, and, through the agency of steam, hydrogen will be added.

Some of the refuse will be deposited on the cracking plate 19, or the molten metal 19′, above it, and from which it can be removed from time to time by cooling the furnace, withdrawing the oil from the cracking chamber 18, and dome D, then opening ports 52, which are more clearly shown in Figs. 2 and 4, and with a narrow scraper, or long slicing chisel, clearing the surface of the plate or the metal.

In Fig. 3, a detailed drawing shows a form of vapor or liquid trap tank and release pop valve herein 59, is the container or tank provided with a tightly fitting cover 59′, held in place by means of bolts. A bottom plate 59″, is provided and attached in a similar manner so as to make a perfectly tight inclosure.

The release pop valve 58, is arranged centrally on pipe 24, and the spring 58″, can be regulated for various pressures by means of the rod and cross head 58′, which projects through the cover 59′, and is properly sealed by a gland or stuffing box. Oil or vapors escaping through the release pop valve 58, and collected within tank chamber 59, can be discharged through pipe 25 and valve 62.

This description applies also to pop valve 12, in tank 13, valve 32 in tank 31, and to valve 63 in tank 64.

The condensing apparatus, E

As this process of oil conversion is continuous, newly admitted oil to chamber 18, will in turn be "cracked" and changed in the apparatus into lighter and more volatile products, which will pass off in the form of vapors through goose neck 34 and 35. These will enter the condenser head 37, of apparatus E, and be led down through the coil pipes 42, where condensation takes place, and the accumulated distillate will escape through valve 63, in trap tank 64, then pass off through pipes 65 and 72, into collecting tank F, or it may be drawn off through pipe 66, and valve 67, or trapped in tank 90, then released through sight box 69, and collected in tank F.

A column 68, on which glass gages 70 and 71, are located, is mounted in close proximity to tank 43 of condensing apparatus E, in order to accurately record the height of accumulated oil in the lower part of coil pipes 42, or if trapped in tank 90, the glass gage 90′, will indicate the height of oil therein.

Release valves 39 and 40, are mounted near the top of this column, which is connected to condenser head 37, by means of pipe 38, as safety devices, in emergency, to relieve excessive pressure.

Collecting tank, F

Distillates which are withdrawn from condensing apparatus E, can be accumulated in a suitable containing device such as collecting tank F, into which they can flow through pipe 72 and be withdrawn from the tank by means of pump 74 and pipe 73.

It may here be stated, that since this process of oil conversion depends upon subjecting the oil or oily vapors to very high temperatures considerably above their vaporizing or boiling points, and since this heat cannot be applied without volatilizing in unconverted form, certain portions of the original oil or oily vapors which condense in the upper part of dome D, the trap tank 31, and pipe 33 provision is made for the oil to be return-d to the converted or supply system through pipes 75, and collecting chamber 76, pipes 29, 77 and 78′, which latter takes into the neck pipe 20.

Inasmuch as the precise degree of temperature at which the plate 19, is maintained in practice, will largely depend upon and be varied by the gravity and boiling point of the oils to be treated, and other conditions, it will be sufficient to state that the temperature of the plate will be maintained at a cracking temperature of sufficient intensity to bring about the desired conversion of oil or oily vapors while under heavy vapor pressure throughout the system from the source of supply through to the end of or beyond the condenser and liquid traps.

There are various parts of apparatus not as yet described, but which will be more fully enumerated in the [fol. 1252] several hereinafter modes of operation; and while the above described apparatus may be modified greatly and yet be well adapted to carry out my process, I have designed and constructed the converter so that it may be operated in the following manner.

Mode of operation (atmospheric)

When converting very low boiling point oils and vapors, or those above 65° B. under atmospheric conditions, and with only a light vapor pressure in the system, oil is admitted to container A, through pipe 1, the displaced air passing out through pipe 2, at the top, until a sufficient quantity of oil is stored for progressive work.

The system is then supplied with oil through valves 3 and 4, pipes 7 and 8, passing valves 9, and entering coils 15, of preheater B, interposed between the oil supply tank A, and converter C—D.

The oil circulating through these coils, is heated by the overflow hot oil from dome D, contained within the tank 16, then passes through coil 17, in stack 50, where it receives an additional heating by means of the waste heat from furnace C, and is then passed through pipe 53, into cracking chamber 18, of the converter C—D, where a portion of it is brought into contact with the intense cracking heat maintained in plate 19.

The oil is held at a uniform surface level in dome D, as indicated by a dotted line X, for the purpose of supplying weight to hold the body of oil down against cracking plate 19, and also to provide a medium for the partial arrest of up-flowing converted and volatilized vapors, which

are rapidly evolved by subjecting the oil to intensely high temperatures.

As the vapors rise through pipe neck 20, to escape into the dome D, an intense agitation is carried on within this pipe, and which would cause undue and undesirable agitation over the surface of oil at line X, if it were not checked by the perforated baffle plates 56, located within this neck.

As the oil rapidly becomes heated and volatilized, and would expand to unreasonable bounds if confined into the dome D, for any prolonged length of time, the overflow pipes 75, are provided to carry off the surplus unconverted oil, which flows down through them, into connecting chamber 76, and out through pipe 24 and valve 81, sight box 82, pipe 25, and into pre-heater tank 16, from which it overflows at the top into pipe 27, and is accumulated in tank 26, from which it may be withdrawn through pipe and valve 83, by pump 84, and returned to reservoir tank A, by means of pipe 85.

This returned oil may then be supplied again to the converter through the system just described.

The overflow pipes 75, are attached to base plate 96 (Fig. 6), and are located within the lower part of dome D, as to very effectually help in the evaporation of vapors which, having been generated in cracking chamber 18, rise through the oil in neck pipe 20, and that contained in the lower part of dome D, where they partially condense.

The heat of the contained oil within the dome D, drives them into vapor form again, and a certain portion is driven off from the surface of the oil at X. The action takes place so rapidly within the dome, however, that some of the converted unvolatilized oils would be carried away in an ordinary single pipe drain, and to prevent this undesirable condition, the series of stand pipes 75, are so arranged on the base plate 96, and located at the bottom of dome D, as to make ample provision for the escape of such vapors from the increased surfaces presented by the multiple of pipes and their inner superficial area.

This pipe arrangement is more clearly shown in Fig. 6, which affords a sectional view of the base plate 96, the stand pipes 75, and the chamber 76, provided with the draw off pipe 24.

A certain portion of oil, having been "cracked," converted and vaporized, rises to the top of dome D, and passes out through pipes 33 and 29, through valve 36, and goose

neck pipe 35, to condenser E, where, in the pipe coils 42, immersed in cold water, the vapors are reduced to condensate or distillates which pass out through pipe 66, valves 67, sight box 64, and pipe 72, into collecting tank F, from which the oil may be withdrawn through pipe 73, by means of pump 74, and delivered as required, through discharge pipe 85.

An important feature of pre-heater B, is the expansion tank 91, located above it, and also the vent pipe 86 above it, through which air and gases may pass to avoid vacuum or pressure within the tank 16, and which would interrupt the proper flow of hot oil through the apparatus.

Another feature of importance embodied in this system is the series of water and sediment traps 88, 89 and 90, located at principal discharge points, so that any foreign matter or substances contained in the oil may precipitate out and not interfere with the perfect operation of the process.

Mode of operation (partial pressure)

If a light or medium vapor pressure of not more than two or three atmospheres, or about 50 pounds to the square inch above that of the atmosphere, is required in a part of the conversion system, when operating on low boiling point oils or oily vapors, the valve 36, in gooseneck pipe 35, of the vapor line is closed, also valve 81, in pipe 24, of the hot oil [fol. 1253] overflow, under dome D, valve 77′ in pipe 77, and valve 4, in pipe 7, of the supply apparatus A; thus closing the system from pump 5, to pop valve 32, in tank 31, and pop valve 58, in tank 59.

The release pop valve 12, in tank 13, is set by means of the stem 12′, to record a required pressure on the gage 11, and the pump 5, is operated to withdraw oil from the container A, and force it through pipe 10, against a vapor pressure greater than that which is maintained in the converter dome D, and at which pressure it will be released through pop valve 12, collected in trap tank 13, and by gravity flow, returned to contained A, through pipe 14.

When this supply system under pressure, is in operation, oil is admitted through pipe 8, and precision valves 9, into the pre-heater coils 15 and 17, and to the cracking chamber 18, by means of pipe 53, and oil inlet 53′, (Fig. 2).

As the heat from plate 19, expands the oil into vapors and volatilizes the same, the converted vapors evolved therefrom

are checked by valve 32, and the overflow hot oil by pop valve 58.

By the proper adjustment of these valves with the stems 32′ and 58′, any required vapor pressure can be had within the container D, according to the nature and gravity of the oil to be operated upon and if such vapor pressure should be required at 50 pounds, as registered on gage 87, then the pop valve 12, should be set to resist a greater pressure, and the pump 5, operated to deliver oil at higher pressure into the system than that of the vapor pressure resistance it will meet with in the cracking chamber 18, and dome D, against which the oil is forced by pump 5.

As a means instrumental in observing these pressures, gages 11 and 87, are provided in order to properly set the controlling springs or weights of the pop valves in the oil and vapor discharge trap tanks 31 and 59.

Oil which is withdrawn from container A, and delivered into cracking chamber 18, by means of pump 5, is driven off in part through dome D, in the form of vapors, and the balance in partially or wholly unconverted hot oil and condensed oily vapors.

That certain portions of oil which, having come in more or less contact with heated plate 19, and becomes vaporized and cracked, rises through neck 20, and body of oil contained in the lower part of dome D, and expanding into the upper part of the dome, is driven off through pipes 33 and 29, pop valves 32, trap tank 31, and goose neck pipe 34, then condensed under vapor pressure in the coils of apparatus E, from which the condensate or distillate flows through pipe 66, valves 67, sight 69, and pipe 72, into collecting tank F, from which it may be withdrawn as heretofore described.

That part of the unvaporized oil which overflows from the surface level X, in the dome D, is conducted through pipes 75, and into chamber 76, from which it is forced, by the vapor pressure in dome D, through pipe 24, release pop valve 58, and is trapped in tank 59, from which it flows by gravity through pipe 25, sight box 82, pre-heater tank 16, and finally into receiving tank 26, from which it may be withdrawn and returned to supply tank A, if desired.

Mode of operation (high vapor pressure)

When operating under high vapor pressure brought about by the expansion, vaporization and retention of oil and oily

vapors in dome D, due to the applied heat to plate 19, as in a steam boiler, and it is desirable to place the entire system under high vapor pressure for the purpose of converting high boiling point hydro-carbons by the application of intense heat and pressure above that of the atmosphere, valve 4, in pipe 7, is closed, and the release pop valve 12, in tank 13, is set against a pressure sufficient for the pump 5, to deliver oil into the chamber 18.

The pop valve in tank 59, is opened wide, the valve 62, in pipe 25, and valve 81, in pipe 24 is closed.

Pop valve 32, in tank 31, and valve 36 in pipe 35, are both opened wide to allow a passage of vapors in free communication with the condensing apparatus E.

Pop valve 63 in tank 64, is set against a vapor pressure by means of stem 63′, and precision valves 67 are closed, while valve 77′ in pipe 77 is opened, thus effectually sealing the system from pump 5, or source of supply, to the pipes 65 and 72, at the end of the condensing apparatus E, which constitutes the discharge outlets for the condensate.

Valves 3 and 6, are then opened and pump 5, is operated to augment the flow of oil into the converter C—D, where the method of oil circulation and vapor collection, with the system under high vapor pressure, is the same as heretofore described when operating under atmospheric or partial and light vapor pressures.

In the discharge of overflow hot oil, however, through pipe 24, and pop valve 28, the accumulation of oil is registered in the glass gage 92, located on collecting tank 59, from which tank it can be withdrawn through valve 62, as it may be required, to keep the oil at a uniform surface level at x, in dome D, and not to flood the trap tank 59. In like manner, the accumulated condensate in the lower part of coils 42, of condensing apparatus E, can be seen in glass [fol. 1254] gages 70 and 71, located on column 68, and by means of pop valve 63, in tank 64, or by opening precision valves 67, in pipe 66, the oil in the lower part of the condensing coils 42, may be kept at a desired level. Distillates can also be accumulated under high vapor pressure in running tank 90, on which glass gage 90′ is located, and released through valve and pipe 72′ into tank F.

The sight boxes 82 and 69, are provided as a means of inspecting the discharge of oils from the system, and together with the glass gages and pressure registering gages,

they form an important part of the visible registry methods for determining the proper speed and flow of oil through the system.

Gases which may be present in the distillate, or fixed gases made in the process of conversion, can escape through pipe 93 and valve 94, leading out from trap tank 64, or through pipe 93′ in trap tank 90.

As the condensate collected in tank F, is of a complex nature, composed of converted and some partially converted original oil, it may be withdrawn and treated by any of the common methods of fractional distillation or "topping," and the residue returned to the container A, if desired, for re-treatment as before.

From the foregoing disclosures, it is apparent that I have succeeded in formulating an apparatus and method of operation which is well suited to my process of oil and oily vapor conversion, and which is readily adapted to the several objects in view, and that, as a result, I have made it possible with this apparatus, to convert inexpensive available hydrocarbon oils into products of greater commercial value, as well as to increase the yield of petroleum and aromatic oils to meet market conditions.

As many changes could be made in the above described construction and methods of operation, and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limited sense.

It is also to be understood that the language used in the following claims is intended to cover all of the generic and specific features of this invention, and all statements of the scope of the invention which, as a matter of language, might be said to fall there between.

Having described my invention what I claim as new and desire to secure by Letters Patent is:

1. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining a portion of the oil relatively separate and distinct from the main body of the oil, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for introducing superheated steam into said

oil at the point where the cracking temperature is applied, and means for collecting and condensing the generated vapors.

2. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining the lower portion of the oil relatively separate and distinct from the main body of the oil above, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for maintaining vapor pressure on said oil during the cracking operation, and means for collecting and condensing the generated vapors under pressure.

3. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining the lower portion of the oil relatively separate and distinct from the main body of the oil above, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for maintaining vapor pressure on said oil during the cracking operation, means for introducing superheated steam into said oil at the point where the cracking temperature is applied, and means for collecting and condensing the generated vapors under pressure.

4. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining a portion of the oil relatively separate and distinct from the main body of the oil, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for continuously introducing oil into said body of oil at the point where the cracking temperature is applied, means for maintaining a predetermined vapor pressure on said body of oil, and means for condensing the generated vapors.

5. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining the lower portion of the oil relatively separate and distinct from the main body of the oil above, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for continuously introducing oil and superheated steam into said body of oil at the point where the cracking temperature is applied, means

for maintaining a predetermined vapor pressure on said body of oil, and means for condensing the generated vapors.

6. In a device of the class described, the combination with [fol. 1255] means for confining a body of oil, means for subjecting a portion of said oil below the surface to a local cracking and converting temperature, means for continuously introducing oil into said body of oil at the point where the cracking temperature is applied, means for maintaining a predetermined vapor pressure on said body of oil, means for automatically drawing off any surplus unconverted oil to maintain said body at a substantially constant level, and means for condensing the generated vapors under vapor pressure.

7. In a device of the class described, the combination with means for confining a body of oil, of means for subjecting a limited portion of said oil at the lower part of said body to a local cracking temperature, means for continuously supplying preheated oil to said limited portion of oil where the cracking temperature is applied, means for drawing off oil from the upper portion of said body to maintain the level, and means for condensing the vapors of the converted oil.

8. In a device of the class described, the combination with means for confining a body of oil, of means for subjecting a limited portion of said oil at the lower part of said body to a local cracking temperature, means for continuously supplying preheated oil and superheated steam to said limited portion of oil where the cracking temperature is applied, means for drawing off oil from the upper portion of said body to maintain the level, and means for condensing the vapors of the converted oil.

9. In a device of the class described, the combination with a container for a body of oil embodying means for maintaining a flat shallow portion of the oil at the bottom relatively separate and distinct, of means for subjecting said flat shallow portion of oil to a cracking temperature, means for maintaining vapor pressure on the oil during the cracking operation, and means for condensing the generating vapors under pressure.

10. In a device of the class described, the combination with a container for a body of oil embodying means for

maintaining the lower portion of the oil relatively separate and distinct from the main body of the oil above, of means for subjecting said separate portion of oil to a local cracking and converting temperature, means for continuously introducing oil and superheated steam into said body of oil at the point where the cracking temperature is applied, means for maintaining a predetermined vapor pressure on said body of oil, means for condensing the generated vapors, and means for maintaining a predetermined pressure on said vapors during condensation.

11. In a device of the class, described, the combination with a converter, means for supplying oil to said converter under pressure, means for heating the oil in said converter to a cracking temperature, a condenser connected to said converter, an adjustable automatic pressure control valve in said connection between said converter and said condenser, an outlet from said condenser, and an adjustable automatic pressure control valve in said outlet.

12. In a device of the class described, the combination with a converter comprising a lower cracking chamber of limited capacity, an upper expansion dome of greater capacity, and a connecting pipe or neck, of means for supplying oil and superheated steam to said cracking chamber, means for applying intense heat to said cracking chamber to convert the oil therein, means for maintaining a substantially constant oil level in said dome, and means for removing and condensing the vapors passing into said dome.

13. In a device of the class described, the combination with a converter comprising a lower cracking chamber of limited capacity, an upper expansion dome of greater capacity, and a connecting pipe or neck, of means for supplying oil and superheated steam to said cracking chamber, at a point where the cracking temperature is applied, means for applying intense heat to said cracking chamber to convert the oil therein, means for maintaining a substantially constant oil level in said dome, and means for removing and condensing under self-generated vapor pressure the vapors passing into said dome.

14. In a device of the class described, the combination with a converter comprising a thin horizontal cracking chamber having a flat bottom plate adapted to be raised

to a high temperature and a central neck extending upwardly, an oil and vapor dome or receptacle into the bottom of which said neck leads, and means for supplying oil to said cracking chamber.

15. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil and vapor dome above said chamber into the bottom of which said neck leads, and means for introducing oil and superheated steam into said cracking chamber through the top.

16. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil and vapor dome above said chamber into the bottom of which said neck leads, means for introducing oil and [fol. 1256] superheated steam into said cracking chamber through the top, means for drawing off vapors from the upper portion of said dome, and means for drawing off oil from said dome to maintain the level therein.

17. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil and vapor dome above said chamber into the bottom of which said neck leads, means for introducing oil into said cracking chamber through the top, means for drawing off vapors from the upper portion of said dome, means for drawing off oil from said dome to maintain the level therein, and means in said neck and dome to prevent the vapors rising up into said dome from unduly agitating the oil therein.

18. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil

and vapor dome above said chamber into the bottom of which said neck leads, means for introducing oil and steam into said cracking chamber through the top, means for drawing off vapors from the upper portion of said dome, and a series of draw-off pipes extending from the bottom up into said dome to the desired oil level.

19. In a device of the class described, the combination with a converter including a thin horizontal cracking chamber having a flat bottom plate, means below said plate for subjecting it to high heat, means for supplying oil and steam to said chamber through the top, and a metal in said chamber on said plate having a fusing point below the cracking point of the oil to be treated.

20. In a device of the class described, the combination with a converter including a vapor dome, of a condenser, a pipe connection between the vapor space of said dome and said condenser controlled by a manually operated valve, a second pipe connection from the vapor space of said dome to said condenser, an automatic pressure regulating valve in said second connection, and means for controlling the discharge from said condenser.

21. In a device of the class described, the combination with a converter, including a vapor dome of a condenser, a pipe connection between the vapor space of said dome and said condenser controlled by a manually operated valve, a second pipe connection from the vapor space of said dome to said condenser, an automatic pressure regulating valve in said second connection, an outlet at the bottom of the condenser controlled by a manually operable valve, and a second outlet from the bottom of said condenser having therein an adjustable automatic pressure regulating valve.

22. An apparatus of the nature disclosed, comprising in combination an oil supply tank and preheater, a converting chamber connected therewith and means for supplying and regulating the entry of unconverted liquids and oils to same, an overlying inclosed expansion dome for the collection of partly or wholly converted oily vapors in the upper part and unconverted oil in the lower part of said dome, means for the withdrawal and condensation of said vapors under vapor pressure, means to withdraw unconverted hot liquid oil from the lower part of said dome through a circumfer-

entially arranged series of over-flow pipes attached to the bottom of said dome, means for utilizing said hot overflow oil in said preheater to heat incoming cold oil before entering said converting chamber and means for returning said oil with newly admitted oil to the action of intense heat in said converting chamber and vapor dome.

23. In a device of the class described, the combination with an oil converting chamber, of an expansion dome above said chamber and in communication therewith, means for drawing off converted vapors from the upper part of said dome, and a series of overflow pipes projecting into said dome at the bottom to withdraw surplus unconverted oil and maintain its level.

24. In a device of the class described, the combination with an oil converting chamber, of an expansion dome above said chamber and in communication therewith, a circumferentially arranged collecting chamber below said dome, means for withdrawing converted vapors from the upper part of said dome, and a series of circumferentially arranged overflow pipes for unconverted oil projecting upwardly into said dome and communicating with said collecting chamber.

25. In a device of the class described, the combination with an oil converter adapted to be raised to a cracking temperature, means for supplying oil to said converter, an expansion dome overlying said converter and in communication therewith, means for withdrawing converted vapors from said dome, means for permitting the overflow of hot unconverted oil in said dome to maintain the level therein and means for importing heat from said overflowing hot oil to the oil being supplied to the converter to preheat the same.

26. In a device of the class described, the combination [fol. 1257] with an oil converter adapted to be raised to a cracking temperature, means for supplying oil to said converter, an expansion dome overlying said converter and in communication therewith, means for withdrawing converted vapors from said dome, means for permitting the overflow of hot unconverted oil in said dome—to maintain the level therein, means for imparting heat from said overflowing hot oil to the oil being supplied to the converter to preheat the same, and means for returning said overflowing oil to the converter with fresh oil.

27. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil and vapor dome above said chamber into the bottom of which said neck leads, and means for introducing oil into said cracking chamber.

28. In a device of the class described, the combination with a thin horizontal cracking chamber having a flat bottom plate, means below said plate for heating it to a temperature sufficient to crack or convert oil in contact with it, a central neck leading upwardly from said cracking chamber, an oil and vapor dome above said chamber into the bottom of which said neck leads, and means for introducing oil into said cracking chamber, a collecting chamber around said neck below said dome and overflow pipes extending from said collecting chamber into said dome and terminating at the desired oil level therein.

In testimony whereof I affix my signature.

Joseph H. Adams.

Witnesses: Joel S. de Selding, A. Capstick.

[fol. 1258] PETITIONER'S EXHIBIT 188

J. H. ADAMS.

PROCESS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED MAR. 30, 1911. RENEWED APR. 17, 1919.

1,327,263. Patented Jan. 6, 1920.

2 SHEETS—SHEET 1

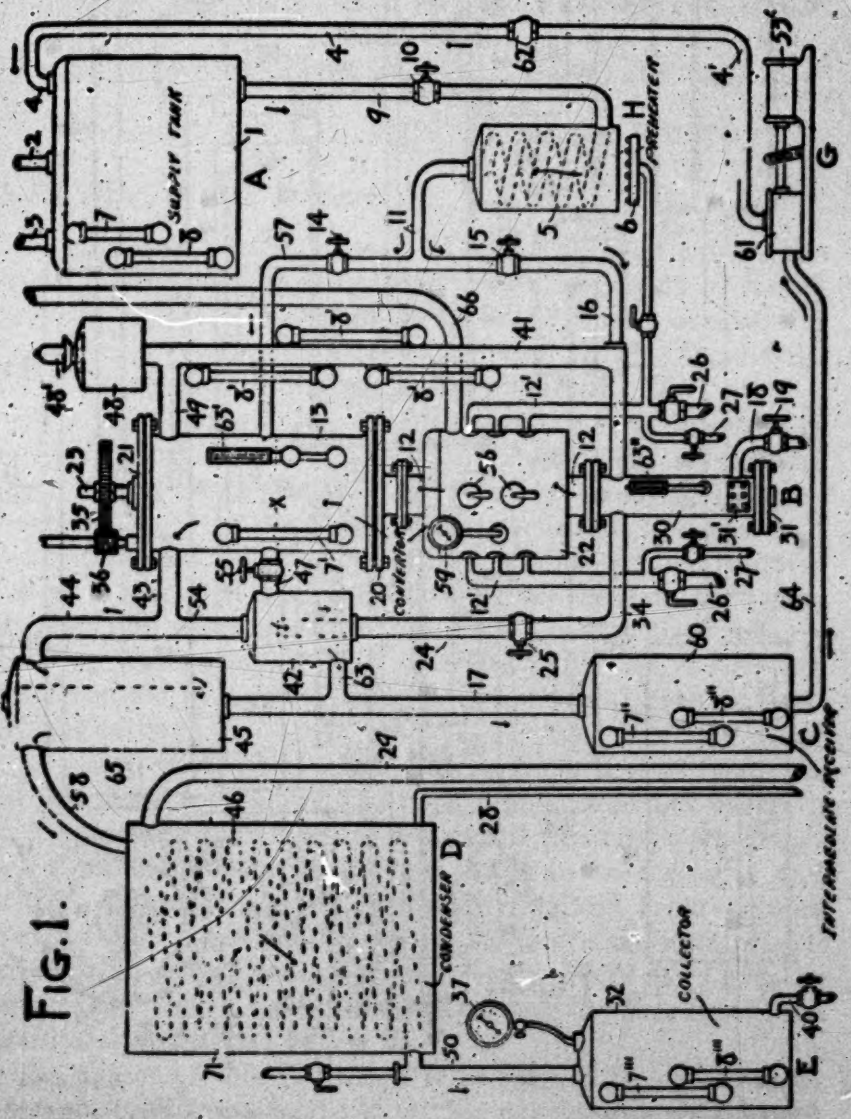

FIG. 1.

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[fol. 1259]

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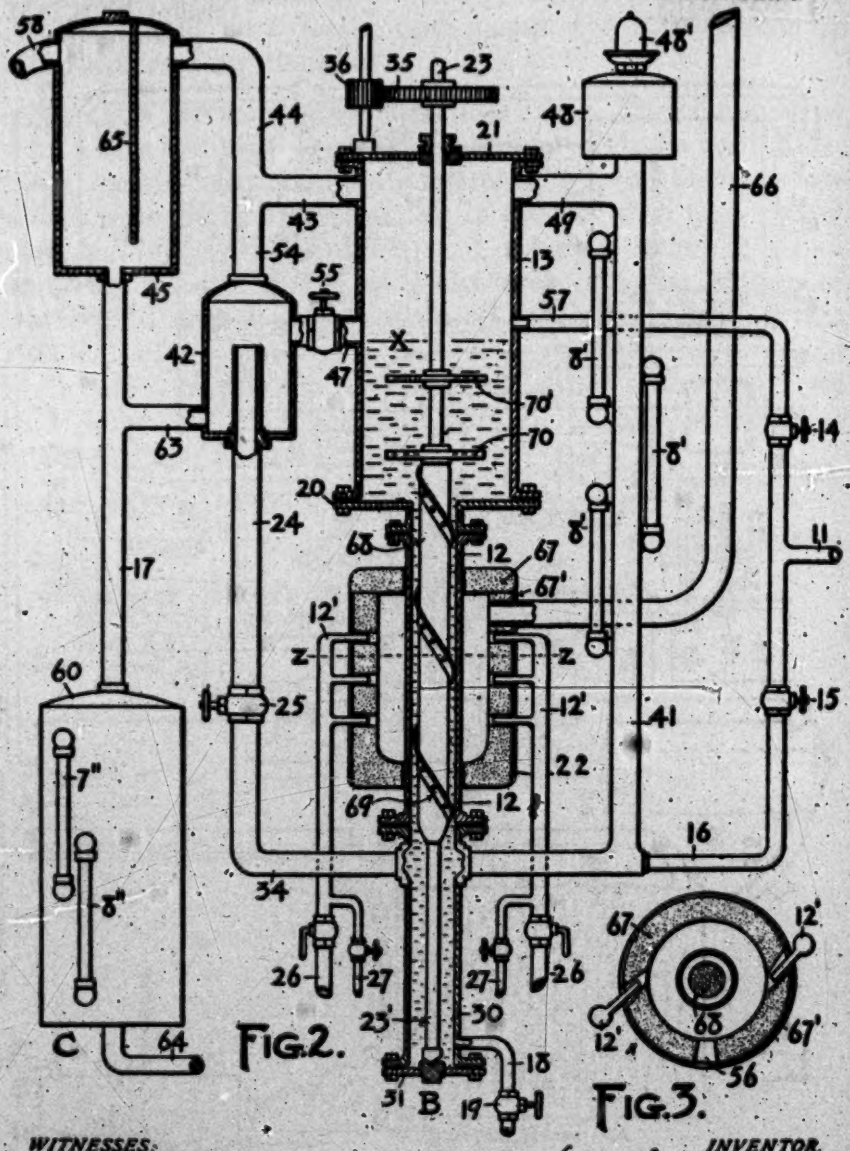
PROCESS FOR THE CONVERSION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED MAR. 30, 1911. RENEWED APR. 11, 1919.

1,327,263. Patented Jan. 6, 1920.

2 SHEETS—SHEET 2.



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Process for the Conversion of Liquids, Fluids, and Oils

1,327,263. Specification of Letters Patent. Patented Jan. 6, 1920

Application filed March 30, 1911. Serial No. 618,011.

Renewed April 11, 1919. Serial No. 289,425

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented a new and useful Process for the Conversion of Liquids, Fluids, and Oils, and of which the following is a specification.

This invention relates broadly to the art of essentially converting fluids, such as oils, into products of a dissimilar character, in contradistinction from fractional distillation processes, but in its more intense aspect it consists in a thermal method of converting more or less refined mineral hydro-carbon oils, such as those of the benzin, kerosene, gas and fuel oil series into the more volatile products resembling light oils, benzins and the naphthas, which are characterized by a lower specific gravity and greater commercial value.

It is also within the scope of this invention to treat the various crude petroleums having asphalt and tar bases in such a manner that the oils driven off in vapors when collected and condensed will have a lower specific gravity and greater volume than the products obtained from similar crude oil by any of the known methods of fractional distillation, while at the same time the residues will have greater commercial value than those obtained by the fractional distillation methods.

One object of this invention is to formulate a process of a commercially practical nature for carrying out the above stated conversion or transformation (as clearly distinguished from a mere distillation) by means of externally applying a high degree of heat to a chamber composed of

a heat enduring material maintaining a pressure in said chamber, while containing hydro-carbon oils, and heating the walls of said chamber to an incandescent temperature of sufficient intensity to locally crack and convert the said oils into oils or oily spirits essentially different in nature from untreated oils, the pressure being maintained while the cracked vapors are being condensed as hereinafter explained. By the term vapor I mean the gaseous form of a substance which is normally liquid at ordinary atmospheric temperature.

As conducing to a better understanding of the ultimate basis of this invention, it may here be recalled that crude petroleum, by a process of fractional distillation, may be separated into a multitude of component parts comprising spirits, oils, heavy bottoms and residues differing from one another in insensible gradations.

Commercially, the distillation of crude oil is not carried to extreme limits of refinement, the aim being to produce the maximum yield of the three principal products for which there is the greatest demand.

Of these, kerosene 43° to 47° Baumé gravity constitutes about 60% of the crude petroleum (Pennsylvania); naphtha of about 62° gravity Baumé 4% of the crude petroleum; "automobile naphtha," "stove naphtha" and others called "gasolene" ranging from 64° to 85° gravity Baumé, about 10% of the crude petroleum and the balance, or about 26% of crude petroleum, represents the heavy bottoms from which the lubricating oils and wax are obtained and the residues of pitch, or coke, if the distillation is carried to extreme limits.

Owing to the somewhat unsettled state of the nomenclature of mineral oils, these products are sometimes given modified names, particularly with regard to the "gasolene" series which at the present time is extensively sold under Baumé gravities considerably less than was the custom a few years ago.

The fact remains, however, that these products, no matter how they be named or classed, are not usually single distinctive oils, but as ordinarily found in commerce are in reality unseparated mixtures of higher and lower gravity oils having their component parts so proportioned that their average gravity conforms to the Baumé gravities by which the various by-products of the crude petroleum are known

commercially as lubricating, fuel, gas and kerosene oils, benzins, naphthas and gasolenes.

Thus, an analysis by fractional distillation will show each of these commercial products to consist of a multitude of fractions ranging through a wide scale of gravities from the semi-solids below 25° gravity Baumé to the most volatile spirits in the neighborhood of 85° gravity Baumé and [fol. 1261] slightly higher, although those which form the greater proportion of any one product will possess gravities within a range from 10 to 20 points in the Baumé scale and approximately the gravity of the product.

The ordinary process of fractional distillation will not accomplish the results which constitute the objects of this invention since that process merely serves to more or less perfectly separate the oils (which may be regarded as mechanical mixtures) into their component parts.

However, by the herein disclosed process discovered by me, it is now quite feasible to convert a high specific gravity oil of the benzin, kerosene, gas and fuel oil types into a lower specific gravity oil or petroleum spirit mixture such as benzine, naphtha or so called "gasolene".

This I accomplish by subjecting the oil or mixture of oils to the powerful influence of pressure and a properly applied external decomposing temperature varying in intensity according to the character of the particular oil undergoing treatment.

In one part of the process of refining oils by fractional distillation, more particularly those of the lower Baumé gravity type, and commonly known as "tar", the oil is heated in the "tar" still to a temperature of approximately 1000° F. to more or less perfectly break up the heavier molecules.

This, however, is a distinct operation from my process where I employ an intense temperature and pressure in breaking up the high boiling point hydrocarbons into those of lower boiling points to increase the yield of gasolenes and naphthas, the pressure being maintained during condensation of the lower boiling point hydrocarbons as hereinafter explained.

The nature of the process is such that its full disclosure may be greatly facilitated by describing certain characteristic features of an apparatus adapted to carry out the same, in conjunction with the statements detailing the

manner in which the oil will course through and undergo essential change in quality in the various parts of the apparatus.

In the drawings, like character of reference denote corresponding parts through the several views of which: Figure 1 is an assembly in elevation of the apparatus as designed for commercially carrying out my process.

Fig. 2 is a sectional elevation showing one of the many possible forms of converter which may be employed for externally subjecting oil to a cracking or decomposing temperature by the application of an intense heat to the exterior walls of an oil containing chamber composed of heat enduring material.

Fig. 3 is a horizontal section taken through 65 line *x*—*x* of Fig. 2.

Referring now to Fig. 1, A represents a suitable supply apparatus which serves as a source of the oil which is to be converted.

As will be understood, this oil supply apparatus may assume diverse forms, but that shown in the drawing will be found quite suitable for ordinary usage.

In this embodiment, the containing vessel 1 of the supply apparatus A may be somewhat elevated with respect to the adjacent converter B so that the gravitating tendency of the oil may augment its flow into the converter B under the influence of the more or less weight of oil in the tank and pressure which may be maintained over it, notwithstanding the compression which may be maintained over the surface of the oil in the converter.

The fluid oil may be admitted into the containing vessel or tank 1 by means of one or more suitable supply pipes indicated by 2, while at the same time the displaced air may escape through pipe 3, from the top of tank 1, or pipe 3 may be connected with a suitable air compressor so that a pressure may be maintained over the surface of oil contained in tank 1 to further augment the flow of oil from the tank to the converter B.

Such tank 1 may also be provided with suitable glass sight gages 7 and 8 if desired, and in like manner, gages 7′ and 8′ may be provided on the adjacent converter B.

A pipe 9 connects the supply tank 1 with the oil heater H in any desired manner, then from the heater the heated oil is conducted through pipe 11 to converter B, as shown.

It is best to heat the oil before it is admitted to the converter B so that the heat from the furnace of the converter may be conserved for the more important function of cracking, splitting the molecules of and rapidly vaporizing the oil, and therefore the oil heater H is provided in which the oil may be brought to any desired temperature within the container 5 by gas blast from jets 6, or by other economical means of heating.

The oil heater H is placed in the piping system between the source of oil supply A and the converter B.

The figures of the drawing show one of the many diverse forms which the converter may assume within the contemplation of this invention, and such converter here shown comprises a chamber 12 of heat enduring material and a covered containing vessel or liquid and vapor dome 13, closed at the top by means of cap 21.

The supply pipes 9 and 11 lead the oil to pipes 16 and 57 governed by hand valves 15 and 14 through either one of which oil is admitted to the chamber 12 and lower part of dome 13. These sections may be connected with the gage column 41 on which the glass sight gages 8′ are arranged so that the condition and disposition of the contents [fol. 1262] of the converter may always be the more readily apparent and be susceptible of an intelligent variation by operating the hand valve 10 for regulating the flow of original oil through the supply pipe 9.

The vapor dome 13 may also be provided with a gage glass 7′ for comparative observation.

At the lower part of the converter B and connected to chamber 12 a heavy bottoms and residue chamber 30 is arranged to collect the precipitated carbon and foreign substances thrown down by this converting process, and near to the lower end a suitable drip or outlet pipe 18 may be provided and controlled by the valve 19, shown in Fig. 1 and Fig. 2.

The bottom of chamber 30 is closed by a plate 31 and a hand hole plate 31′ by means of which the chamber may be emptied of its more solid contents and cleared of any sediment which may accumulate therein.

The closed containing vessel or vapor dome 13 is secured to the heat enduring or cracking chamber 12 by means of a

suitable interposed flange member 20 which is securely bolted to each of these respective sections.

Inasmuch as the vapors rising into and filling the upper part of the vapor dome 13 may, at any time, be so rapidly evolved as to exert an undue pressure, I have arranged a compression tank 48 and pop valve 48′ in relation with the upper part of the cylinder or vapor dome 13 by means of the pipe 49 so that any sudden pressure above a given number of pounds to the superficial inch will cause the spring check in the seat of pop valve 48′ to rise and release the excessive pressure.

In other words, by fixing the upper limit of pressure in the apparatus the evolved vapors maintain a predetermined desired pressure therein, the evolved vapors being solely relied upon in accordance with the preferred embodiment of my invention as actually used in practice, before my original application S. #535,879 was originally filed and on which this application was primarily based.

Of course, the converter and fittings are made up as tight as possible and, therefore, I have used between the several flanges and caps, gaskets of asbestos and other oil and heat resisting and indestructible materials, so that the possibility of leakage may be obviated so far as may be necessary from a practical standpoint.

A feature of primary importance is the means for externally applying heat of intense temperature to the oil while contained in the heat enduring chamber 12 when under compression above that of the atmosphere for the purpose of bringing about a conversion of such oil.

Preferably this feature is operated by gas and air blast under pressure and comprises one or more jets 12′ through which a proper mixture of gas and air is forced and ignited to form the necessary elements of combustion.

The nozzles of these jets are projected through openings or ports into an inclosed retort 22 composed of fire brick or fused quartz linings 67 held together within a strong and suitable metallic shell 67′, as shown in Fig. 3, and provided with an exhaust pipe 66 to lead out the spent gas and fumes of combustion.

This inclosed retort is designed to conserve the greater part of the intense heat from the several gas jets 12′ for the purpose of maintaining the walls of the heat enduring chamber 12 at a temperature of sufficient variable inten-

sity; to crack or decompose oils of varying characteristics which may be contained within the chamber.

In the shown form this retort 22 with its intake pipes 26 and 27 and outlet or exhaust pipe 66 is made up in circular form to inclose the greater part of the cylindrical heat enduring chamber 12 and, while this precise form may be varied to conform to the different shapes and designs in which retorts can be made commercially available for this purpose, the form shown in Figs. 1, 2 and 3 will be found very suitable for converting many classes of petroluem oil. This retort or furnace 22 and heat enduring chamber 12 are especially adapted for the economical use of a mixture of gas and air under pressure as an intense heating fuel, and while this unit B is but one form of converter, a number of such units in series would possess commercial advantages.

The gas and air being brought in separately through pipes 26 and 27 become mixed within the pipe leading to the jets 12'.

When this combustible mixture is ignited the heat action within the retort 22 and the color of the walls of the heat enduring chamber 12 may be observed through the sights ports 56, located in the walls of the retort 22, and indicated also by the pyrometer 59 located in a central position on the retort, where the thermal end may extend into the body of the generated heat within the inclosure.

For the preservation of the heat enduring chamber 12 and the distribution of heat generated within the walls of the retort 22 the jets 12' are arranged to enter the ports in the walls of the retort at a tangent whereby a circulating heat may be distributed about the exterior walls of chamber 12, as indicated in Fig. 3, instead of the jets being projected directly at local parts of the cracking chamber 12 with chances of possible destruction.

This form of intense heater is especially adapted for [fol. 1263] working in the oil and gas regions where the cost of natural gas is very low or the gas manufactured in gas producer plants and fuel oil is inexpensive, or where cheap gas is not obtainable then the form of heater may be changed to conform to the available fuel or means of heat generation to carry on this process.

The oil containing and cracking chamber 12 may be constructed of various heat enduring metals, alloys, carbons,

graphites, graphitic carbon and other materials known to withstand a constant or varying temperature of high intensity, but as the structural character of such a part does not relate specifically to a process invention it will be unnecessary to elaborate thereon in this process disclosure.

This intense externally applied heat affects the contained oil in such a manner as to very efficiently convert the same and is thus adapted to assist in a step of primary importance to my process.

It may here be stated that, when operating upon certain classes of oils, that is, the more volatile oils and spirits, it is highly desirable to localize the application of the external heat so as to prevent the spread, so to speak, of the heat in a lower degree of intensity throughout the mass than is necessary to efficiently "crack" the oil, but of sufficient intensity to cause an evaporation of undue amounts of the oil at a distance from the intensely heated walls of the cracking chamber without bringing about a conversion.

To this end, in the embodiment of the apparatus shown by Fig. 2, I have provided a cylindrical core or sheath 68 of a size designed to fill a larger part of the central space within the cracking chamber 12 and to displace a considerable amount of oil which would otherwise be contained therein, thereby compelling such oil as may be located between this core 68 and the containing chamber 12 to come into more or less direct contact with the intensely heated walls of the cracking chamber 12.

This core 68 is supported by the rods 23 and 23', the whole forming a shaft which by means of a bearing in cap 31 at the bottom of heavy bottoms chamber 30 and a packed bearing or gland in the vapor dome cap 21, may be caused to revolve when the gears 35 and 36 arranged above the crown of the vapor dome 13 are operated upon by power.

A helical collar or worm 69 of metal or other suitable material is attached to the periphery of the core 68 but in such a manner as not to directly engage the interior surfaces of the cracking chamber 12.

This core-cylinder and collar, when revolving, agitates the oil contained within the cracking chamber 12 and causes it to be thrown into more or less close proximity to the intensely heated walls of the chamber for the purpose of cracking, splitting the molecules of and otherwise convert-

ing all or as much of the original oil as may be possible during the accelerated movements within and passage through the chamber.

Another specific function of the helical collar 69, when in rotation, is to remove and throw down the accumulation of scales and articles of carbon and coke which may adhere to the interior surfaces of the cracking chamber 12.

From this it will be understood that whenever the fluid to be converted is admitted to the chamber 12 and containing-vessel 13 and brought to the proper and safe level, as indicated by the dotted line X in the dome 13, and also indicated in the gages 7′ and 8′, it is in a position to be operated upon by the externally applied intense heat which will be maintained within the retort, and in close relation to the original oil through the walls of the cracking chamber and which, when evolved as vapors, will be constantly and uniformly replaced by fresh quantities of untreated and non-converted oil.

In other words, the oil contained within the channel between the core 68 and chamber 12 will be held in place by the head weight of oil contained in the lower part of vapor dome 13 thus preventing the intense heat from so rapidly volatilizing the small amount of oil in this channel and driving it away from the intensely heated walls of the chamber, before additional oil could be supplied to take its place, that burning or searing could result from the ignition of superheated oil vapors which might at times become mixed with air or other re-active agents.

The retort 22 being preferably constructed of suitable heat resisting and conserving material, admirably serves to localize the intense heat just where it is most needed, i. e. in the immediate vicinity of the more or less central part of the cracking chamber 12.

On the other hand, the unconverted oil contained in the lower part of vapor dome 13 does not become heated to such a degree as to cause undue evaporation but allows the lighter and more volatile oils to pass through it and escape to the top of the dome in the form of vapors from which they pass out through pipe 43 while the unconverted heavier oil is discharged through pipe 47 into liquid trap 42.

From the foregoing it will be seen that during the maintenance of high temperature within the retort, for the pur-

pose of intensely heating the walls of the cracking chamber while containing oil, the effect of this heat is to cause the [fol. 1264] oil which is in the immediate vicinity of the internal walls of the chamber to be broken up or converted into oils having a lower specific gravity.

The action is extremely violent, causing the "cracked" oil to become immediately vaporized and the uprising of this vapor brings about a furious local agitation within the cracking chamber and the contained oil.

In order to prevent excessive agitation and to prevent particles of oil being projected above the body of fluid in vapor dome 13 and allowing them to drop back again into the heated mass and thereby causing a deteriorating reaction, perforated baffle plates 70 and 70′ are located on the rod or shaft 23 and made fast so that they occupy a position within the body of oil, as shown in Fig. 2. It may also be mentioned that owing to the excessive quantity of heat, and owing also to the fact that much of the heat will radiate at a diminished temperature into surrounding portions of the oil more distant from the incandescent walls of the cracking chamber, considerable oil may and will be volatilized without undergoing conversion, just as illuminating oils and naphthas are boiled and vaporized without essential conversion in the ordinary process of fractional distillation. By operating apparatus under pressure, however, I am able to reduce the undesirable volatilization without conversion to a minimum, and as a consequence the oils are in a large proportion "cracked" or otherwise converted in character.

Oil will be constantly flowing toward and into contact with the walls of the cracking chamber 12 to take the place of that already vaporized.

This newly admitted oil will in turn be "cracked" and changed in the apparatus into lighter or more volatile products.

Thus, the complex mixture of oils, known commercially as "distillates" of benzin, kerosene, gas and fuel oils, may be changed or transformed by means of my process into a mixture of lighter oils and spirits which bear a general resemblance to and have the properties of that which is known as illuminating oil, naptha and gasoline.

It may be mentioned also that during this operation, the raw non-converted oils will be relieved of more or less of the carbon of which they are in part composed, as well as some of the foreign substances which it is desirable to eliminate.

This, of course, alters their chemical character and converts them from one or more of the products of the hydrocarbon series into those of lower specific gravity and possibly different character. The carbon which is removed in this manner will be in part deposited upon the hot walls of the cracking chamber and in part precipitated in the adjacent oil, being to some extent held in suspension and to some extent gravitating through the oil toward the heavy bottoms chamber provided for its accumulation.

When operating in this manner it has been observed that apparently only a certain part of the fluid ultimately evaporated comes in direct contact with the highly heated walls of the cracking chamber, for the reason that the condition of the heat is sufficient to evaporate a certain somewhat remote portion of the oil at a lower temperature than is required for "cracking" the oil.

Accordingly, the vapors passing into the dome 13 will be composed not only of the oil which has suffered a breaking up of its molecules and deposition of a part of its carbon by the high converting heat, but will also contain a certain portion of the unchanged original oil in the form of vapor.

These mixed vapors are evolved very rapidly owing to the high temperature of the cracking chamber and consequently care should be exercised to keep the oil level line in the dome 13 at the proper mark in the glass gages and not permit it to fall below or approach a line which borders on or approaches near to the walls of the cracking chamber and which might be followed by searing or burning the oil and destroying it for commercial purposes.

The mixed vapors pass from the dome 13 into discharge pipe 43, and thence through the pipe 44 to a vapor trap 45 in which a baffle plate 65 is arranged in such a manner as to make it necessary for the light vapors to descend nearly to the bottom of the trap on one side of the plate and rise again on the other before they can escape through the goose neck 58 to the condensing apparatus D.

Vapors not light enough to rise in pipe 44 are condensed, then conducted to a liquid trap 42 through the pipe 54, and in like manner vapors not light enough to rise in the vapor trap 45, after descending along the baffle plate 65, fall to the bottom of trap 45 and the condensate is led through pipe 17 into the receiving tank 60 of apparatus C, which is provided with glass sight gages 7″ and 8″, and from which it may be withdrawn and returned to the supply tank 1 by means of the suction pump 61 of apparatus G and the pipe 64.

By means of the pump operating mechanism 53 the oil is conveyed through return pipe 4′ and 4 in which the check valve 62 is located to relieve the back pressure on the pump, and finally the oil is admitted through the top of tank A, as the original oil was let in through pipe 2.

The lighter mixed vapors pass from the trap 45 through the goose neck 58 and into a suitable condensing coil of pipe [fol. 1265] 46 immersed in a water tank 71 forming a part of the condensing apparatus D of Fig. 1.

This apparatus D is provided with a cold water supply pipe 28 and an overflow pipe 29 whereby a continuous flow of cold water can be maintained within the tank 71 for the purpose of bringing about a complete condensation of vapors passing through the coils of pipe.

Since some of the vaporized original unconverted oil may tend to condense before reaching the condensing apparatus D, I prefer to connect the bottom of pipe 54 with the liquid trap 42 so that condensate may be led through pipe 63 into pipe 17, the upper end of which is in turn connected with the bottom of vapor trap 45, so that all condensate not accumulated through condensing apparatus D may be returned to tank 1 after it is collected in receiving tank 60 of apparatus C.

In this manner the already-condensed unconverted oil may be passed into the cracking chamber again without first being mixed with and separated from the converted condensed oils in apparatus D by a fractional distillation method.

After passing through the coil condenser and cooling tank apparatus D, the fluid oil passes through pipe 50 into the apparatus E of which tank 32 provided with glass gages

7''' and 8''', is the container and from which it can be withdrawn by means of cock 40, shown in Fig. 1.

For the treatment of certain oils it is necessary to maintain a more or less complete compression of one or more atmospheres in the apparatus from the source of supply to the end of or beyond the condenser in conjunction with the other features of my invention, for thereby I am enabled to retard to a certain extent the overproduction of vapors and the volatilization of oil that must necessarily be held in check within the cracking chamber 12 until as much of the "cracking" operation can be performed on the contained fluid as experience and practice warrants.

Furthermore, the vapor compression in connection with the treatment of certain oils will promote uniformity and certainty in the satisfactory operation of the process, and therefore, the compression in addition to normal atmospheric pressure becomes an important feature in this process.

Thus, from practical experience, it has been found that a pressure maintained over a body of oil contained in the converter retards the vigorous volatilization of the lighter vapors in a desirable manner, assists in the conversion of oil and renders a more uniform flow of product therefrom.

On the other hand, a greater pressure maintained over a body of oil contained within the converter and throughout the system from the source of supply to the end of or beyond the condenser when treating and converting low Baumé gravity oil helps materially in this process of conversion.

The composite oil withdrawn from tank 32 may either be directly returned to the converter in order to still further decompose the same into lighter products, or it may be subjected to fractional distillation or other operations to more or less completely segregate its components, and such components as may not be of the desired quality may then be returned to the converter for further treatment.

When treating oils of different gravities, it may be desirable to cause them to flow either upward or downward through the cracking chamber 12, and for this purpose intake pipes 16 and 57 are provided.

When fluid is admitted through the lower part of apparatus B, valve 14 in pipe 57 and valve 25 in pipe 24 is closed.

Valve 15 in pipe 16 and valve 55 in pipe 47 is opened thereby allowing the oil to flow through pipe 16 into the lower part of the converter.

By the continuous method of supply and discharge, the unconverted oil which has not been driven off in vapors flows out through pipe 47 into liquid trap 42, then through pipe 63 into pipe 17 and down into tank 60.

When oil is admitted to the upper part of converter B through pipe 57, valve 15 in pipe 16 and valve 55 in pipe 47 is closed and valve 25 in pipe 24 is opened.

The head weight and pressure on the oil in the lower part of vapor dome 13 causes the oil to flow down through cracking chamber 12 and out through pipe 34.

It is then forced up through pipe 24 and over into liquid trap 42 and flows out through pipe 63 into pipe 17 from which it is discharged into tank 60.

For the purpose of determining the proper speed at which the oil should flow through converter B, the thermometer 63′ is located near the lower external part of vapor dome 13, and to determine the nature of the heavy bottoms in chamber 30 the thermometer 63″ is located on the chamber so that the registered heat will enable an oil operator to know when to withdraw some of the contents.

The above specifically described apparatus may, of course, be modified greatly and yet be well adapted to carry out one or more of the essential correlated steps of my process.

It is apparent that I have succeeded in formulating a process well suited for achieving the several objects and ends in view, and that as a result I have made is possible [fol. 1266] to readily convert comparatively inexpensive commercially available oils into products of greater value.

In view of the foregoing disclosure, it will be obvious to those skilled in the art of oil refining that my process may be carried out with different fluids from those specified herein, by varied steps, and with the assistance of different apparatus without, however, departing from the scope of my invention, and accordingly I intend that all matters contained in the above description shall be interpreted as illustrative and not in a limited sense. Inasmuch as the precise degree of temperature at which the walls of the cracking chamber should be maintained in practice, will largely depend upon

and be varied with particular conditions, such as the compostion of the raw oil to be converted, and it will be sufficient to state that the temperature will generally vary from a low red to a full white or incandescent heat, according to the nature of the fluid to be treated.

It will of course be understood by those skilled in the art that the temperature at which the walls of the cracking chamber become incandescent will vary in accordance with the material of which it is composed and it will further be understood that the temperature necessary to secure the desired cracking of the oils will vary with the character of the material under treatment. The terms "incandescent," "a low red," and "a full white heat," as above used, are therefore not to be considered as terms of limitations upon the use of the process since it will be understood from the nature and purpose of the process that the essential point in this respect is merely that the temperature of the oil in the chamber be raised to the temperature at which the desired cracking will take place.

I desire it to be understood also that the language adopted in the following claims is intended to cover all of the generic and specific features of the herein disclosed invention, and all statements of the scope thereof which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:-

1. A process of treating high-boiling hydrocarbon oils to convert a relatively large percentage of the same into lower boiling hydrocarbon oils which consists in continuously supplying the high-boiling hydrocarbon oils to a closed chamber subjecting the high boiling hydrocarbon oils in liquid form to a cracking temperature in said closed chamber under pressure to evolve vapors of the desired lower boiling hydrocarbon oils and condensing said vapors by passing them through connections to a condenser, all of the connections to and through the condenser being in open communication so as to insure a substantially uniform pressure from the heater to the condenser.

2. A process of converting oil which consists in subjecting the oil to a cracking temperature under pressure in a closed chamber, supplying oil to said chamber during the

cracking operation to maintain a body of liquid therein, and condensing the evolved vapors of the cracked or converted oil by passing said vapors through connections to a condenser all of the connections through and to the condenser being in open communication so as to insure a substantially uniform pressure from the heater to the condenser.

3. A process of treating high-boiling hydrocarbons to obtain a realtively large yield of lowed-boiling hydrocarbons, consisting in continuously admitting the high-boiling hydrocarbons from a supply to a closed chamber, subjecting a body of liquid hydrocarbons in said chamber to a cracking temperature under pressure, and condensing the evolved vapors of the cracked or converted oil by passing said vapors through connections to a condenser all of the connections through and to the condenser being in open communication so as to insure a substantially uniform pressure from the chamber through the condenser and drawing off the residue and returning it to the supply.

4. The method of treating hydrocarbons of high-boiling point to obtain hydrocarbon oils of lower boiling point which consists in heating the high boiling hydrocarbons in liquid form to a cracking temperature in a chamber under pressure and condensing the cracked vapors produced by passing the same from the said chamber to a condenser, supplying hydrocarbons of high-boiling point to said chamber during the cracking operation to maintain a proper supply therein, separating heavier products from the cracked vapors at a point between said chamber and said condenser and maintaining the connection from said chamber to and through the condenser in open communication so as to insure substantially uniform pressure from the chamber through the condenser, and returning said heavier product to said chamber whereby the desired low boiling hydrocarbon oil is continuously and ultimately produced.

5. A method of converting oils which consist in continuously feeding oil under pressure to a chamber, heating said oil in liquid form in the chamber to a cracking temperature while maintaining a vapor pressure on said oil in said chamber, condensing the vapors generated, by passing

them through connections to a condenser all of the connections to and through the condenser being in open communi- [fol. 1267] cation so as to insure a substantially uniform pressure from the chamber through the condenser, withdrawing lighter condensate from the condenser, and returning heavier condensate to the said chamber for repetition of the treatment, whereby a lighter condensate is continuously produced as the ultimate product.

6. A process of converting oil which consists in causing oil to flow from a source of supply in a confined liquid stream restricted in cross section, heating said liquid stream to a cracking temperature, thereby generating vapor pressure, and condensing the cracked vapors by passing them under substantially the same pressure at all points through a condenser in open communication with said stream of oil, whereby low boiling or converted oil is continuously produced and collected as an ultimate product in said condenser.

7. A process of converting oil which consists in maintaining a body of oil in a pipe-like heater, heating said oil in liquid form in said heater at a cracking temperature, maintaining vapor pressure on said oil while being subjected to the cracking temperature and condensing the vapors generated by passing them under substantially the same pressure at all points through a condenser, whereby lower boiling or converted oil is continuously produced and collected as an ultimate product in said condenser.

8. A process of converting oil which consists in continuously passing oil in a relatively thin stream under pressure through a pipe-like heater to a larger container or vapor dome in open communication therewith, heating said oil locally as it passes through said pipe-like heater to a cracking temperature, maintaining substantially the same vapor pressure on said oil in said heater and vapor dome and conducting off and condensing the vapors in said dome.

9. A process of converting oil which consists in continuously passing oil in a relatively thin stream under pressure through a pipe-like heater to a larger container or vapor dome in open communication therewith whereby the pressure will be substantially the same in said heater and dome,

heating said oil locally as it passes through said pipe-like heater to a cracking temperature, passing the vapors from said dome through connections to a condenser all of the connections to and through the condenser being in open communication so as to insure a substantially uniform pressure from the heater through the dome and condenser.

10. A process of treating high boiling hydrocarbons to obtain lower boiling point hydro-carbons which consists in continuously supplying the high boiling point hydro-carbons to a closed chamber, subjecting the high boiling hydro-carbons to a cracking temperature in said closed chamber under pressure, removing carbon from the heated portion of said heated chamber and passing the vapors evolved through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the condenser.

11. A process of treating high boiling hydro-carbons to obtain lower boiling point hydro-carbons which consists in continuously supplying the high boiling point hydro-carbons to a closed chamber, subjecting the high boiling hydro-carbons to a cracking temperature in said closed chamber under pressure, allowing the carbon produced by said cracking temperature to descend by gravity out of the heated zone and passing the vapors evolved through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the condenser.

12. A process of converting oil which consists in subjecting the oil to a cracking temperature under pressure in a closed chamber, supplying oil to said chamber during the cracking operation to maintain a proper supply therein, removing the carbon from the heated portion of said chamber and passing the vapors evolved through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the condenser.

13. A process of treating high boiling hydro-carbons to obtain lower boiling hydro-carbons which consists in continuously admitting the high-boiling hydro-carbons from a supply to a closed chamber, subjecting the hydro-carbons

in said chamber to a cracking temperature under pressure, removing the carbon from the heated portion of said heated chamber, passing the vapors evolved through connections to a condenser, all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser, and drawing off the residue between said chamber and condenser and returning it to the supply.

14. A process of treating high boiling hydro-carbons to obtain lower boiling hydro-carbons which consists in continuously admitting the high-boiling hydro-carbons from a supply to a closed chamber, subjecting the hydro-carbons in said chamber to a cracking temperature under pressure, allowing the heavy residue and carbon produced by said cracking temperature to descend by gravity out of the heated zone passing the vapors evolved through connections to a condenser, all in open communication so as to insure a substantially uniform pressure from the chamber [fol. 1268] through the condenser, and drawing off the residue between said chamber and condenser and returning it to the supply.

15. A process of converting oil which consists in causing oil to flow from a source of supply in a confined liquid stream restricted in cross section, heating said liquid stream to a cracking temperature, thereby generating vapor pressure, separating out the heavy residue and carbon and passing the cracked vapors under substantially the same pressure through a condenser in open communication with said oil.

16. A process of converting oil which consists in continuously supplying oil to a pipe-like heater, heating said oil in said heater at a cracking temperature, maintaining vapor pressure on said oil while being subjected to the cracking temperature, allowing the carbon to descend by gravity out of the cracking zone, and passing the vapors generated under substantially the same pressure through a condenser.

17. A process of converting oil which consists in continuously passing oil in a relatively thin stream under pressure through a pipe-like heater to a larger container or vapor dome in open communication therewith, heating said oil locally as it passes through said pipe-like heater to a cracking temperature removing from said pipe-like heater and collecting carbon resulting in said pipe-like heater, maintaining

substantially the same vapor pressure on said oil in said heater and vapor dome and conducting off and condensing the vapors in said dome.

18. A process of converting oil which consists in continuously passing oil in a relatively thin stream under pressure through a pipe-like heater to a larger container or vapor dome in open communication therewith whereby the pressure will be substantially the same in said heater and dome, heating said oil locally as it passed through said pipe-like heater to a cracking temperature, continuously separating out and removing from said pipe-like heater carbon produced in said pipe-like heater, passing the vapors from said dome through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the dome and condenser.

19. A method of converting oils which consists in continuously feeding oil under pressure to a vertically arranged chamber, heating said oil in said chamber above its bottom to a cracking temperature while maintaining a vapor pressure on said oil in said chamber, allowing the carbon to descend by gravity to the bottom of said chamber beyond the heating zone and continuously passing the vapors generated through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser.

20. A method of converting oils which consists in continuously feeding oil under pressure to a vertically arranged chamber, heating said oil in said chamber above its bottom to a cracking temperature while maintaining a vapor pressure on said oil in said chamber, allowing the carbon to descend by gravity to the bottom of said chamber beyond the heating zone, permitting the vapors generated to pass from said chamber, separating the heavier vapors from the lighter converted vapors and passing the lighter vapors through a condenser, the connections through which said vapors pass to and through the condenser being all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser.

21. A method of converting oils which consists in heating oil in a vertically arranged chamber above its bottom to a cracking temperature while maintaining a vapor pressure.

on said oil in said chamber, allowing the carbon to descend by gravity to the bottom of said chamber beyond the heating zone, permitting the vapors generated to pass from said chamber, separating the heavier vapors from the lighter converted vapors and passing the lighter vapors through a condenser, the connections through which said vapors pass to and through the condenser being all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser.

22. A method of converting oils which consists in heating oil under pressure in a vertically arranged chamber above its bottom to a cracking temperature while maintaining a vapor pressure on said oil in said chamber, allowing the carbon to descend by gravity to the bottom of said chamber beyond the heating zone and continuously passing the vapors generated through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser.

23. A process of treating high boiling hydro-carbons to obtain lower boiling hydro-carbons which consists in subjecting the high boiling hydro-carbons to a cracking temperature in a closed chamber under pressure, allowing the carbon produced by said cracking temperature to descend by gravity out of the heated zone and passing the vapors evolved through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the condenser.

24. A process of treating high boiling hydrocarbons to obtain lower boiling hydro-carbons which consists in supply- [fol. 1269] ing the high boiling hydro-carbons to a closed chamber, subjecting the high boiling hydro-carbons to a cracking tmeperature in said closed chamber under pressure of the evolved vapors, moving carbon from the heated portion of said heated chamber and passing the vapors evolved through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the heater through the condenser.

25. A method of converting oil which consists in feeding oil under pressure to a chamber, heating said oil in liquid form in the chamber to a cracking temperature while main-

taining a vapor pressure on the oil in said chamber, condensing the vapors generated by passing them through connections to a condenser, all of the connection to and through the condenser being in open communication so as to insure a substantially uniform pressure from the chamber through the condenser, withdrawing lighter condensate from the condenser and returning heavier condensate to said chamber for repetition of the treatment, whereby lower boiling condensate or converted oil is ultimately produced in said chamber.

26. A process of changing high boiling hydrocarbon oils to obtain lower boiling hydrocarbon oils which consists in subjecting the high boiling hydrocarbons in liquid form in a chamber to a cracking temperature therein, condensing the evolved vapors by permitting them to pass freely to a condenser and maintaining a substantial pressure throughout the cracking chamber and condenser solely by the vapors evolved in the chamber and withdrawing the lower boiling oils from the condenser as the ultimate product.

27. A method of converting oils to obtain a relatively large yield of lower boiling oils which consists in heating the oils to be converted, in liquid form, in a chamber to a cracking temperature while maintaining a vapor pressure on said oils in said chamber solely by the vapors generated therein, and condensing said generated vapors by passing them through connections to a condenser all in open communication so as to insure a substantially uniform pressure from the chamber through the condenser and withdrawing the lower boiling oils from the condenser as the ultimate product.

28. A method of converting oils to obtain a relatively large yield of lower boiling oils which consists in supplying oil to a chamber, supplying heat to a body of oil in liquid form therein at a temperature sufficient to crack the oil, condensing the evolved vapors by continuously passing them to a condenser in open communication with the chamber and confining the evolved vapors for maintaining a material pressure above atmospheric effected by the volatile constituents of the liquid so as to insure a substantially uniform self-imposed pressure from the chamber through the condenser and withdrawing the converted oil from the condenser as the ultimate product.

29. A process of treating high boiling hydrocarbons to obtain a relatively large yield of lower boiling hydrocarbons which consists in subjecting a body of the high boiling hydrocarbons in liquid form to a cracking temperature in a closed chamber, and condensing the vapors evolved by passing them through a condenser in free communication with the chamber and while subjected solely to the pressure of the evolved vapors in excess of atmospheric pressure in the chamber and to and through the condenser and withdrawing the converted oil from the condenser as the ultimate product.

30. A process of converting oil which consists in continuously supplying oil to a pipe-like heater, heating said oil in said heater at a cracking temperature, maintaining vapor pressure on said oil while being subjected to the cracking temperature, allowing the carbon to descend by gravity out of the cracking zone, and passing the vapors generated through a condenser.

31. A method of converting oils which consists in continuously feeding oil under pressure to a vertically arranged chamber, heating said oil in said chamber above its bottom to a cracking temperature while maintaining a vapor pressure on said oil in said chamber, allowing the carbon to descend by gravity to the bottom of said chamber beyond the heating zone and continuously passing the vapors generated through connections to a condenser.

In testimony whereof I affix my signature in the presence of two witnesses.

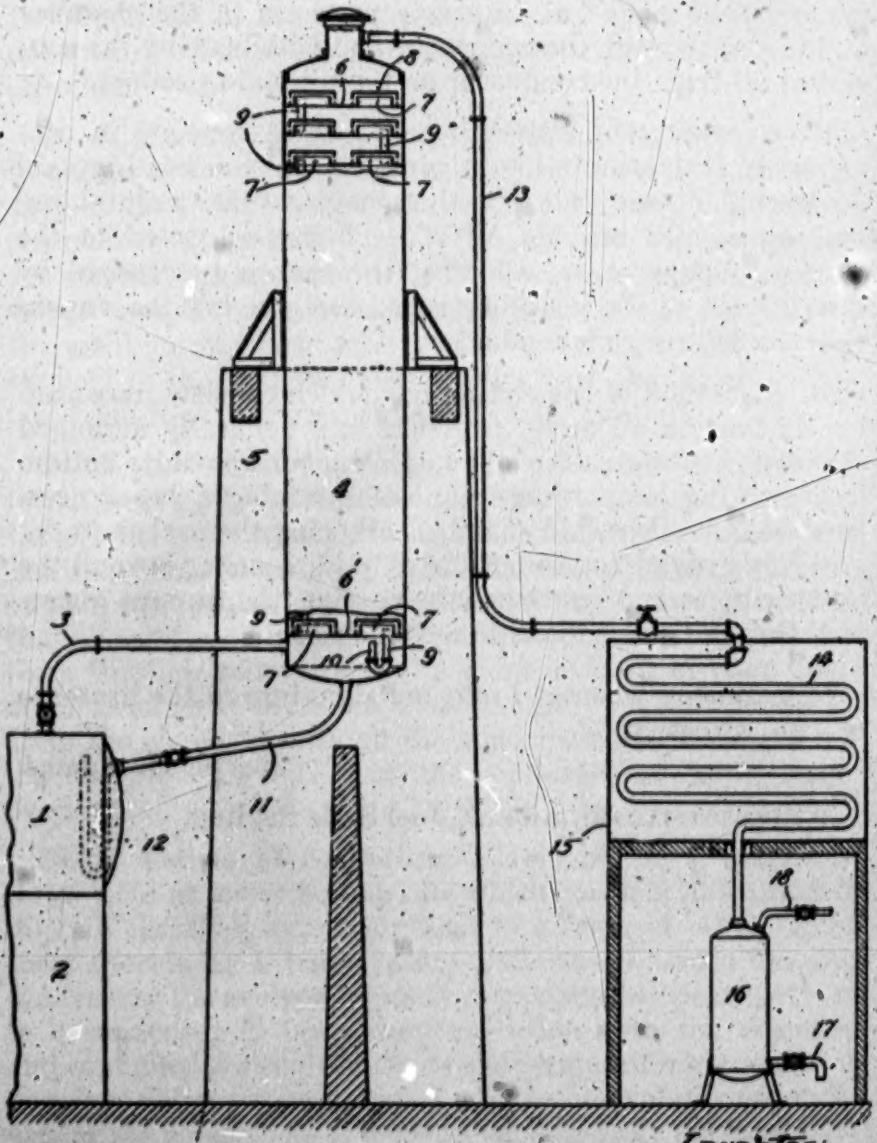
Joseph H. Adams.

Witnesses: Austin Adams, Joel S. de Selding.

[fol. 1270] PETITIONER'S EXHIBIT 189

F. B. LEWIS AND T. S. COOKE.
ART OF DISTILLING PETROLEUM OILS.
APPLICATION FILED MAY 7, 1917.

1,392,584. Patented Oct. 4, 1921.



Witnesses:
E. G. Taylor
Chas. H. Bullock

Inventor:
Frank B. Lewis,
Thomas S. Cooke,
By Bakewell Lay, Cuddy & Wilder
Attys.

[fol. 1271] United States Patent Office

Frank B. Lewis and Thomas S. Cooke, of Whiting, Indiana, Assignors to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Art of Distilling Petroleum-Oils.

1,392,584. Specification of Letters Patent. Patented Oct. 4, 1921.

Application Filed May 7, 1917. Serial No. 166,965.

To all whom it may concern:

Be it known that we Frank B. Lewis and Thomas S. Cooke, citizens of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in the Art of Distilling Petroleum-Oils, of which the following is a specification.

Our invention relates to the art of distilling petroleum oils and more particularly to a process of distillation conducted under pressure for the purpose of effecting the conversion of heavier or high boiling point oils into lighter or lower boiling point oils, as is more fully described in the patent to Wm. M. Burton, No. 1,049,667.

We have discovered that a distillation process of this character may be accellerated and made to yield superior results both quantitatively and qualitatively if the vapors passing from the still are subjected to the absorbing or direct condensing action of a body or bodies of liquid, as for example in a fractionating column or the like. By the use of such a fractionating means there are condensed from the outgoing vapor steam practically all constituents thereof which have not suffered sufficient decomposition, and at the same time the condensing effect is so perfectly controlled that no substantial proportion of the vapors which have suffered sufficient decomposition is condensed. In practice we prefer to connect the inlet end of the fractionating column or its equivalent directly with the still, so that the reflexing condensate may return immediately and continuously to the still. We also prefer to connect the vapor outlet at the top of the fractionating column or its equivalent, through an open pipe, directly with a water cooled condenser in which the vapors constituting the net result of the process are con-

densed under the same pressure obtaining in the still and its connecting fractionating column.

The invention will be fully understood from the following detailed description of one method of carrying out the same. In this description, reference will be had to the accompanying drawing which illustrates more or less diagrammatically an arrangement of still, fractionating column and final condenser, which we find well suited to the practice of our invention.

In this drawing the numeral 1 designates the rear end of a horizontal, cylindrical still mounted upon a furnace 2. The top of the still near the back has tapped therethrough a vapor outlet line 3 which is connected with the base of a fractionating column 4 supported upon masonry piers 5. The fractionating column illustrated in the drawing is of the outline of a vertical cylinder having arranged in its interior a plurality of pans 6, each of which is provided with vapor ducts 7 capped by heads 8 which are perforated at their side walls near the bottom of the pan. A constant level of liquid is maintained in each pan by means of an overflow pipe 9 which discharges into the next lower pan. The bottom pan designated 6^1 is spaced some little distance above the lower end of the column, and the overflow pipe 9^1 for this pan carries an inverted siphon or trap 10. The reflux condensate collecting in the bottom of the column is returned to the still by a drain pipe 11 tapped into the back head of the still and connecting within the still with an inverted siphon 12 (shown in dotted line) by which the reflux condensate is carried down near the hot bottom of the still and again brought upwardly and discharged into the upper portion of the still at a point above the average liquid level and not substantially below the highest liquid level therein.

From the upper end of the fractionating column the outgoing vapors are carried through a line 13 to a condensing coil 14 mounted in a water bath 15. This coil drains into a receiving drum 16 provided at the bottom with a liquid drawoff pipe 17 and at the top with a valved gas-escape and control pipe 18.

The operation of this apparatus is as follows:

A charge of relatively heavy or high boiling hydrocarbon oils from which it is desired to produce a maximum quantity of relatively low boiling point or light hydrocarbons, is introduced into the still 1 and by means of the furnace 2 the contents of the still are raised to the temperature at which

distillation begins. It may be noted that in order to prevent the distillation of any part of the charge contained within the still 1 before the desired operating temperature has been reached, it is of advantage to introduce into the still and condenser system, as for instance through the gas pipe 18, an [fol. 1272] incondensable and chemically inert gas in sufficient quantities to create a substantial pressure within the apparatus. An economical method of effecting this result is fully described in the patent to Edgar M. Clark No. 1,129,034. If the still and condenser system be thus charged with gas under pressure, the liquid body within the still is prevented from distilling over until it has been raised in temperature to the point required to begin the conversion. When this temperature (which is dependent upon the pressure maintain in the apparatus) is attained the liquid contents of the still begin to suffer chemical changes by which they are in part converted into lighter and lower boiling point constituents, and such reaction products accompanied and diluted by a greater or less proportion of vapors which have not been decomposed to the full extent desired, pass out through the vapor line 3 and into the base of the fractionating column 4. In their passage upward through the column these vapors are fractionally condensed, the condensate serving to fill the pans 6 and continuously overflowing from each upper pan to the next lower pan and finally into the base of the column, from which the condensate drains through the pipe 11 back to the still 1. By reason of the inverted silphon 12 this reflux condensate becomes heated to the temperature existing in the still by being carried through the liquid body therein and is then discharged near the top of the still. Should there be any water in the reflux condensate it is therefor introduced in such a manner as to avoid thumping.

When the series of pans 6 in the fractionating column 4 has become filled with liquid the outgoing vapors are compelled to bubble through the liquid in these pans successively in order to reach the top of the column. The pans and the liquid bodies therein are automatically maintained at progressively decreasing temperatures from the base to the top of the column, and the condensate in each pan is of correspondingly different gravity and boiling point. By reason of the thorough washing and extensive surface contact of the vapors with the several liquid bodies, we find

that there is effected an exceedingly accurate fractionation. The column is so proportioned and its condensing capacity is such that the liquid body in the lower pan 6[1] does not at any time in the normal operation of the apparatus contain any appreciable proportion or percentage of the low boiling point or light constituents which are to constitute the net result of the process, so, also the contents of the top pan 6 will be substantially an oil slightly higher in boiling point than the end fractions of the product which is to constitute the net result of the process. The intermediate pans will contain in varying proportions, heavy and light or high boiling point and low boiling point fractions or constituents.

The vapors which escape condensation in the column 4 or which are redistilled from the upper pan 6 thereof, pass outwardly through the line 13 and are condensed in the water cooled condenser 14, draining from the latter into the receiving drum 16 from which they are withdrawn at such a rate as to maintain a free space above the liquid level in the drum.

The pressure within the apparatus will be controlled through the gas pipe 18, this pipe serving to vent from the system any excess quantity of incondensable gas formed therein, or to convey into the system incondensable gas from some other source should the production of gas within the system fail at any time to answer the predetermined pressure requirements therein. A simple method of accomplishing this pressure control through the gas-escape pipe 18 is illustrated and described in the patent to Edgar M. Clark above referred to.

The process heretofore described is of the greater technical advantage when applied to the pyrogenesis of gasolene, i. e., the mixture of aliphatic hydrocarbons mainly of the saturated series and boiling between 80° and 400 to 420° F., from the heavier of higher boiling point constituents of crude petroleum, such as fuel oil, gas oil, and the other relatively heavy products or residues of refinery processes boiling in large part at and above 500° F.

As a specific example of the process above described the following may be given:

A still of a capacity of 200 barrels is provided with a fractionating column of the design shown in the drawing,

6 feet in diameter and 30 feet in height and provided in its interior with 20 pans, the liquid depth in each pan being 6 inches. This still is charged with a petroleum oil or petroleum residue, the fractions of which boil between 450 and 750° F., the mixture having a Baumé gravity of about 30°. The distillation is conducted under a pressure of 5½ atmospheres.

While we have described in considerable detail the specific form of apparatus which we find well adapted to the carrying out of our improved process, as well as the details of a particular commercial process in accordance with the invention, it will be understood that this is illustrative only and for the purpose of making clear the nature and mode of applying the invention and that the invention is not to be regarded as limited in scope to the illustrative details given except in so far as such limitation is included within the terms of the accompanying claims, in which it is our intention to claim all novelty inherent in our invention as broadly [fol. 1273] as is permissible in view of the prior art.

What we claim as new and desire to secure by Letters Patent is—

1. The improvement in the art of cracking petroleum oils by distillation under pressure which consists in passing the mixture of sufficiently cracked and insufficiently cracked vapors continuously produced within the still through a plurality of separated bodies of petroleum oil arranged in series and maintained at temperatures such as to condense all insufficiently cracked fractions but not to condense the sufficiently cracked fractions, and condensing and collecting the sufficiently cracked fractions which escape condensation in the said liquid bodies.

2. The improvement in the art of cracking petroleum oils by distillation under pressure which consists in passing the mixture of sufficiently cracked and insufficiently cracked vapors continuously produced within the still through a plurality of separated bodies of petroleum oil arranged in series and maintained at temperatures such as to condense all insufficiently cracked fractions but not to condense the sufficiently cracked fractions, condensing and collecting the sufficiently cracked fractions which escape condensation in

the said liquid bodies, and continuously returning to the still the insufficiently cracked fractions condensed by the said liquid bodies.

3. The improvement in the art of cracking petroleum oils by distillation under pressure which consists in passing the mixture of sufficiently cracked and insufficiently cracked vapors continuously produced within the still through a succession of liquid bodies of petroleum oil maintained at temperatures such as to condense all insufficiently cracked vapors but not to condense the sufficiently cracked fractions, the said liquid bodies being connected and discharging one into the other, in a direction opposite to the flow of vapors, and separately condensing and collecting the sufficiently cracked fractions escaping condensation in said liquid bodies.

4. The improvement in the art of producing gasolene hydrocarbons from relatively heavy hydrocarbons which consists in subjecting such relatively heavy hydrocarbons to distillation under a pressure upward of 4 atmospheres, passing the mixture of sufficiently and insufficiently cracked vapors continuously produced within the still through a succession of liquid bodies of petroleum oil maintained at temperatures to condense all non-gasolenelike hydrocarbons and not to condense the gasolenelike hydrocarbons, and separately condensing and collecting the gasolenelike hydrocarbons.

5. The improvement in the art of producing gasolene hydrocarbons from relatively heavy hydrocarbons which consists in subjecting such relatively heavy hydrocarbons to distillation under a pressure upward of 4 atmospheres, passing the mixture of sufficiently and insufficiently cracked vapors continuously produced within the still through a succession of liquid bodies of petroleum oil maintained at temperatures to condense all non-gasolenelike hydrocarbons, and not to condense the gasolene-like hydrocarbons, separately condensing and collecting the gasolenelike hydrocarbons, and continuously returning the condensed non-gasolenelike hydrocarbons to the still.

6. The improvement in the art of cracking petroleum oils by distillation under pressure which consists in passing

the mixture of sufficiently cracked and insufficiently cracked vapors continuously produced within the still through a succession of liquid bodies of petroleum oil maintained at temperatures such as to condense all insufficiently cracked vapors but not to condense the sufficiently cracked fractions, the said liquid bodies being connected and discharging one into the other in a direction opposite to the flow of vapors, separately condensing and collecting the sufficiently cracked fractions escaping condensation in said liquid bodies, and maintaining the entire system including the final condenser for the cracked fractions under the same pressure.

7. The improvement in the art of producing gasolene hydrocarbons from relatively heavy hydrocarbons which consists in subjecting such relatively heavy hydrocarbons to distillation under a pressure upward of four atmospheres causing the vapors of the sufficiently cracked fractions to pass through a plurality of separated bodies of petroleum oil arranged in a series maintained at successively lower temperatures, that of the final body being sufficient to pass the gasolene of the desired constitution and condensing and collecting the fractions which pass through said liquid bodies.

Frank B. Lewis, Thomas S. Cooke.

[fol. 1274] PETITIONER'S EXHIBIT 190

C. ELLIS.

MAKING GASOLENE SUBSTITUTE.

APPLICATION FILED OCT. 4, 1913.

1,396,999. Patented Nov. 15, 1921

3 SHEETS—SHEET 1.

Fig. 1.

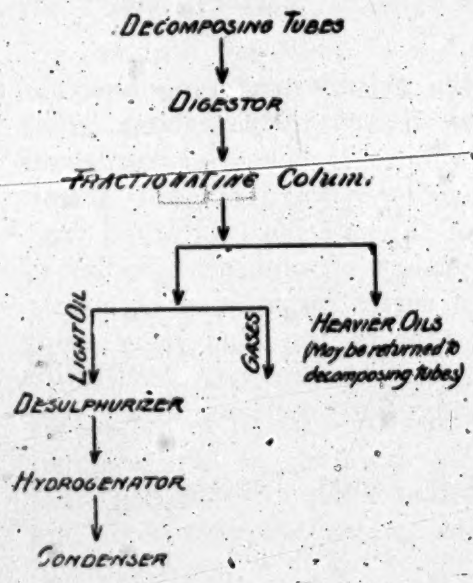
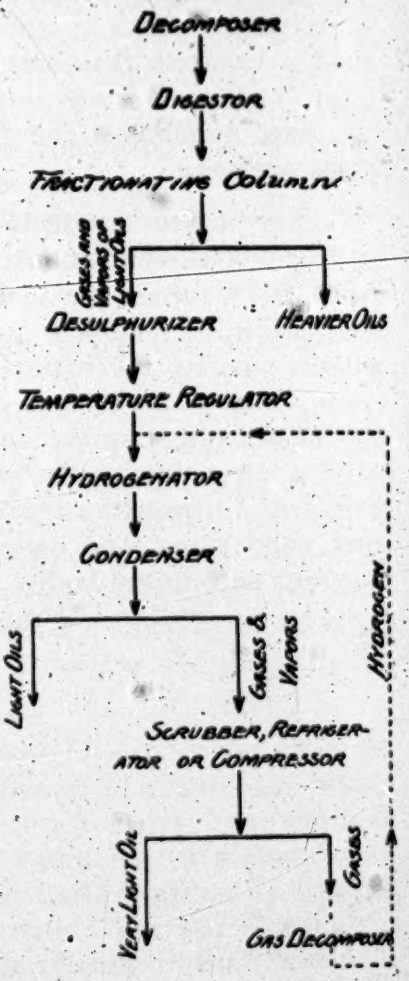


Fig. 2.



Witnesses:

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B. M. Ellis.

Inventor:

Carleton Ellis

[fol. 1275]

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MAKING GASOLENE SUBSTITUTE.

APPLICATION FILED OCT. 4, 1913.

1,396,999. Patented Nov. 15, 1921.

3 SHEETS—SHEET 2.

Fig. 3.

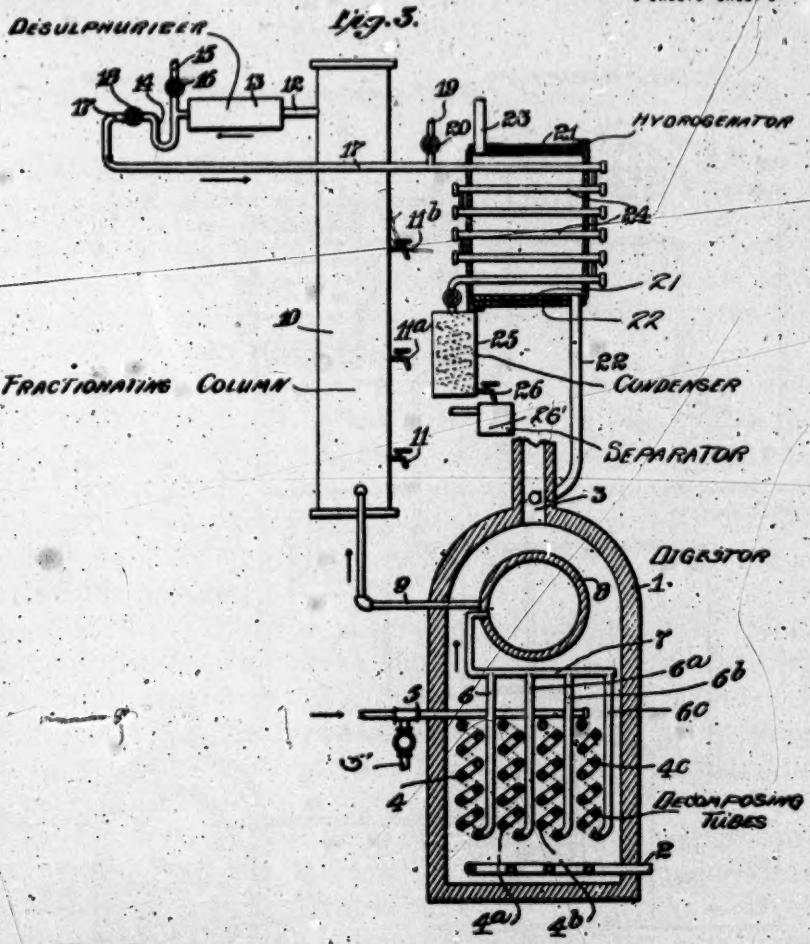

Fig. 4.

Attest:

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B. W. Ellis.

Inventor:

Charles Ellis

4670

[fol. 1276]

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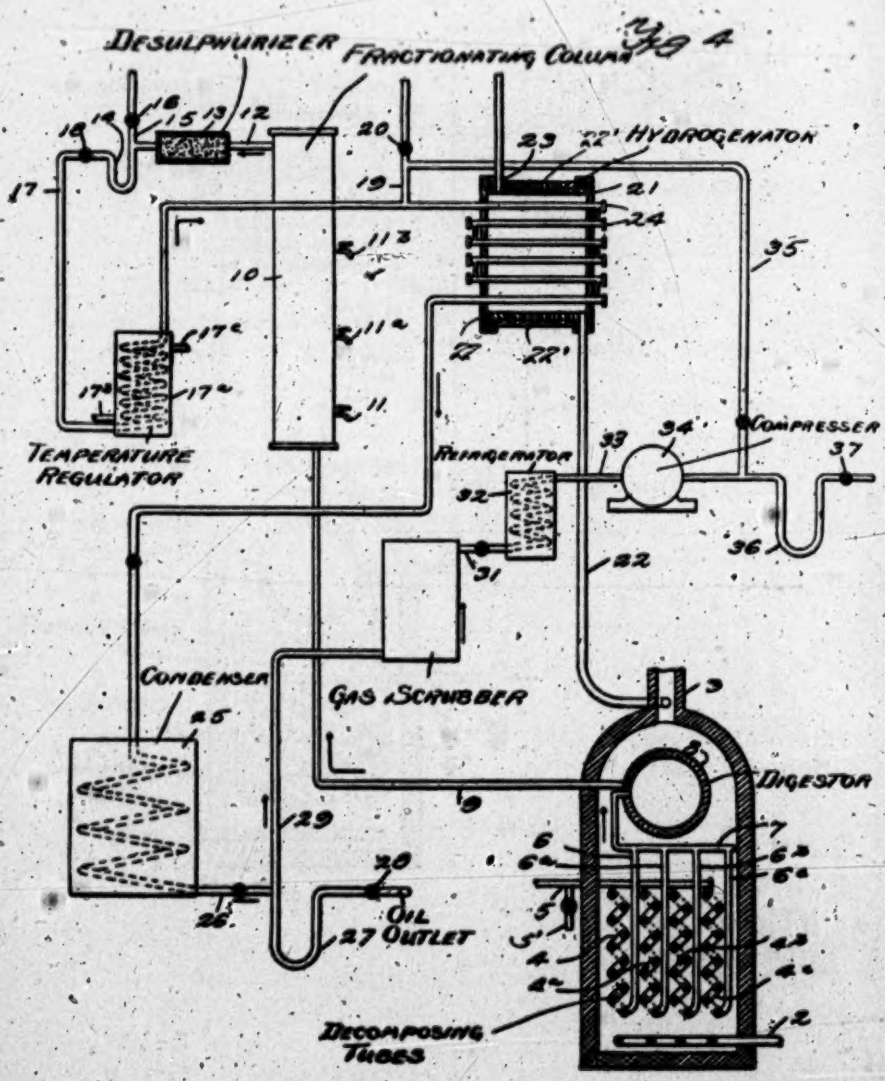
MAKING GASOLENE SUBSTITUTE.

APPLICATION FILED OCT. 4, 1913.

1,396,999. Patented Nov. 15, 1921.

3 SHEETS—SHEET 3.



Inventor,
Carleton Ellis,
By Chas. Fuller
Attorney

[fol. 1277] United States Patent Office

Carleton Ellis, of Montclair, New Jersey

Making Gasolene Substitute

1,396,999. Specification of Letters Patent. Patented Nov. 15, 1921

Application Filed October 4, 1913. Serial No. 793,377

To all whom it may concern:

Be it known that I, Carleton Ellis, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Making Gasolene Substitutes, of which the following is a specification.

This invention relates to a process of making gasolene from heavier oils such as kerosene and the like and is related in particular to a system or organization of correlated elements; the whole forming an integral process or organization whereby from heavier oils there may be obtained lighter fractions akin to or suitable for use in place of ordinary gasolene.

In order to render the nature of the organization clear, I have appended two plans showing the path of material undergoing treatment, this being indicated by Figures 1 and 2; while Fig. 3 shows a structure suitable for carrying out the procedure indicated by Fig. 1 and Fig. 4 apparatus for carrying out the procedure indicated by Fig. 2. Fig. 3 is shown mainly in sectional elevation, and, in a diagrammatic manner, shows the heating and condensing system and stabilizing means adapted for carrying out the present system. Fig. 4 shows in a diagrammatic manner a modified form of the apparatus illustrated in Fig. 3 including also additional apparatus hereinafter referred to in the description of the process indicated by Fig. 2. Fig. 5 is a detail sectional view of one of the decomposing tubes showing the manner in which the catalytic material is placed therein.

By referring to Fig. 1 it will be noted that the first member is a decomposer or decomposing tubes. This element may consist of a series of tubes placed in a furnace and

adapted to be heated to a temperature of 400-600° C., or so, while the heavier oil passes through in the form of a vapor and is subjected to thermal decomposition during such travel. Of course, the tubes may be long or short according to the velocity of travel of the oil vapors with respect to the temperature of the surrounding gases applied for heating such tubes. Into the decomposer may be admitted along with the oil or oil vapors a quantity of steam so as to provide 20-50% of water more or less, based on the nature of the oil employed. In place of a tubular structure a retort or still may be employed. In the decomposing tubes I preferably place catalytic material, preferably metal bodies of a shape adapted to form baffling surfaces while permitting a ready flow of the vapor.

Metal which is a good conductor of heat preferably is employed in order by rapid conduction to prevent a cold core of gases along the middle of the tube rendering that part of the tube without effective action. During the first part of the travel of the oil vapors for effective action I preferably bring them into contact with surfaces of copper and in the latter part of the travel with surfaces of nickel. This may be accomplished by plating "jackstones" and the like with copper or respectively with nickel and packing in the tubes with the pack stones which pack in such a way that the greatest baffling effect is secured at the center and most rapid travel at the circumference of the tube which, of course, is hottest and therefore an automatic equalization of temperature is secured.

A single passage of the heavy oil through the apparatus should yield an amount of light products adapted for use as a gasoline substitute equivalent to from 20 to 40 per cent of the original oil treated. After the oil vapors have been decomposed to the required degree, they are passed preferably to a digester which may be and preferably is a vessel well insulated to prevent loss of heat in which container the heated vapors undergo digestion or reaction among themselves and more or less stabilization with establishment of certain conditions of equilibrium which could not be secured satisfactorily in the decomposing tubes where strong heat is being applied externally.

The decomposition products contain unstable constituents which in the digester, react with the gases present and particularly hydrogen, or with each other or by poly-

merization, to produce more stable compounds in substantial molecular equilibrium. From the digester the vapors may go to a dephlegmator or fractioning column which preferably is of a type used in the rectification of alcohol [fol. 1278] and the like in place of the ordinary coarse dephlegmator used in the present day rectification of oil. In the dephelgmator or fractioning column the heavy oil is condensed and if desired a dephlegmator may be arranged to yield as fractions a gas oil and unconverted kerosene especially if the latter is employed as the raw material. Preferably, however, the kerosene is separated from the heavier oils and the former returned to the decomposing tubes while the latter wihch is preferably separated as a fraction similar to gas oil, is collected and suitable disposition made thereof.

The lighter oils or volatile spirits are not condensed in the dephlegmator and preferably passed into a desulfurator which may be a tube containing copper filings or copper oxid or other metallic or non-metallic desulfuring agent maintained at a temperature suitable for satisfactory desulfurization. Preferably, however, a desulfuring agent similar to that employed in the subsequent process of hydrogenation is made use of.

Oils which have been purified for the market such as, for example, ordinary lamp oil or kerosene contain very little sulfur as a rule, but enough is usually present to affect the catalyzer employed in the hydrogenation step which is subsequently to be described, and in that case the sulfur has to be removed in order to secure a catalyzer of sufficient endurance. When using a catalyzer such as nickel or cobalt, traces of sulfur or chlorin act in a poisonous manner rendering the catalyzer in a short time wholly inert. Oils which have been sufficiently desulfurized for commercial purposes often have enough sulfur or other toxic agents to decrease the catalytic activity, because of the great sensitiveness of these catalytic bodies to catalyzer poisons. Hence if nickel is employed as a catalyzer, preferably the spent nickel catalyzer, that is to say the catalyzer which has lost its catalytic activity, may be employed for removing those traces of divers bodies which act poisonously. While copper oxid and the like will remove

sulfur in a commercially satisfactory way, it is better, as stated, when removing sulfur to fit an oil for catalytic hydrogenation to use as a desulfurizing agent the catalyzer itself or spent masses of the same, as thereby the specific selective action of the metal and removal of the particular traces of sulfur or other toxic agents acting on the catalyzer is satisfactorily effected, which oftentimes may not be the case when using metals or compounds of dissimilar affinities for the sulfur and other toxic agents.

The product having been suitably prepared in this or other manner for hydrogenation, it is now preferably passed through a hydrogenating apparatus in which it contacts with nickel or other catalyzer in the presence of hydrogen. The nickel is preferably carried on a support of the nature of crushed glass or other dense impermeable material. The glass is preferably fairly uniformly plated with a very thin layer of nickel material. A temperature between 200-300° C. preferably is maintained in the hydrogenator during the operation. The product then passed to a condenser where it may be obtained in a suitable form for the market, or, if desired, may be re-distilled or treated with sulfuric acid and alkali or subjected to any other method of treatment, although in general it is sufficient to simply pass the product through the hydrogenator in order to add hydrogen and thereby satisfy the unstable bodies present, as this usually affords a product of good color, odor and stability.

In Fig. 2 the light fraction passes from the dephlegmator uncondensed, the lighter oils and gases being mingled; while according to the plan of Fig. 1, the gas may be removed from the condensed light oils at the dephlegmator. The uncondensed vapors may then pass to a desulfurator and through a temperature regulator where the temperature of the vapor may be adjusted to about 240° C. whereupon they may be introduced into the hydrogenator wherein the free hydrogen contained in the gases of decomposition from the decomposing tubes may be caused to unite with the oil vapors. Hydrogen, of course, may be supplied from an external source in the amount required. The product passes into a condenser and the light oils are thus obtained in a liquid form, while any excess of hydrogen and the other gases which are present containing entrained

vapors may be passed to a compressor or scrubber or washer or refrigerator where any useful light oils may be recovered.

A similar operation may be employed in the case of the gas derived according to the system indicated in Fig. 1. These gases may then be passed through a gas decomposer where they are subjected to a very high temperature in order to break down the hydrocarbons into the carbon and hydrogen and after suitable washing or other purificatin the hydrogen may be returned to the hydrogenator, as described in connection with Fig. 2.

In Fig. 3, 1 is a furnace structure containing a battery of heating tubes as shown at 4, 4^a, 4^b, and 4^c. These consist of pipes set horizontally or practically so, connected end to end in such a manner as to form a continuous passage from the upper horizontal tubes to the lower ones. They are heated by fuel gas supplied through the pipes 2. 3 is a [fol. 1279] chimney for the spent gases or products of combustion. The tubes 4, 4^a, 4^b, 4^c, may be filled with catalytic and heat-conducting material as shown at 3′ (Fig. 5), the uppermost pipes preferably containing copper fragments and the lowermost preferably carrying nickel bodies. A feed-pipe 5 serves for the introduction of oil, oil vapor, oil and water, steam and oil, or the vapors of steam and oil. As shown, a branch pipe 5′ may be provided for the introduction of steam or water, the pipe being provided with a suitable valve to permit regulation of the proportions of oil or oil vapor and water or steam. These pass downwardly through the several series of heating pipes and then by risers 6, 6^a, 6^b, and 6^c, are taken to the manifold 7, which communicates with the digester drum 8. This drum is preferably of considerable length in reference to the diameter and has an inlet for the oil vapors at one end, while the outlet represented in the drawing by 9 preferably is at the other end. The products of combustion from the heaters below the decomposing tubes pass up and around the drum and in some cases may add heat to it and in other cases may serve more as an insulating blanket of heated air to prevent any substantial drop of temperature in the digester 8.

The slow travel of the vapors through the drum enables molecular equilibrium to be established to a considerable

degree. The pipe 9 leads to a dephlegmator 10 which may be a column apparatus of a type adapted to make fairly sharp separation of close boiling fractions. These may be withdrawn at 11, 11^a and 11^b. A pipe 12 carries the light distillate to a desulfurizer 13 which preferably is filled with spent nickel catalyzer. Gases are withdrawn by the pipe 15 which carries the valve 16. 14 is a trap which enables the gases to be collected at that point. 17 is a pipe leading to the hydrogenator 21. The pipe 17 carries the valve 18. 19 is a pipe serving to introduce hydrogen or other suitable reducing gas, the flow of which therethrough being regulated by the valve 20. A flue 22 conducts gases from the stack 3 to the hydrogenator 21 in order to furnish heat for the latter, air being admitted to the hydrogenator by openings, whereby suitable control of temperature is secured which preferably should be between 240-250° C. The hydrogenator as shown consists of a series of tubes 24 connected to form a continuous passage, in the tubes being placed nickel or other catalyzer, but preferably nickel plated or coated on dense impermeable fragments or granules of such a character as to prevent the vapors from permeating the support. The temperature of the hydrogenator may be regulated by admitting any desired quantity of air in addition to the products of combustion from the pipe 22. As shown, the casing 21 is provided with openings 21′ and shutter or valves 22′ are arranged over these openings to permit regulation of the air feed. Thus recovery of the catalyzer when as such it can no longer be used, is made possible, which is difficult when the metal is lodged inside a porous carrier as would be the case with a porous support, causing trouble in regeneration. From the tubes 24, the light oil products are conveyed to a condenser 25 where any remaining condensable fractions are liquefied. The finished product is removed from the condenser by outlet 26, and may be delivered to a separator 26′ for the purpose of removing any excess water. The material obtained from the outlet 26 or the separator 26′ is composed of low boiling saturated hydrocarbons of the nature of gasolene. From the tubes 24 of the hydrogenator 21 the product passes through the condenser 25 provided with the valved outlet 26.

Porous bodies sometimes show a tendency to selectively absorb some portion of the oil, thus tending to clog the

catalyzer. Also in the preparation of the catalyzer with a porous support, it is difficult owing to an occlusive force to free such catalyzer from objectionable impurities by washing. Again there is the difficulty of securing a satisfactory coating of materials; so for these and other reasons a carrier of the nature of glass or metal preferable is employed as a support. Thus iron, copper and aluminum and the like may be employed.

In the somewhat modified form of apparatus shown in Fig. 4, employed in carrying out the procedure indicated by Fig. 2, a temperature regulator 17[a] having an inlet 17[b] and an outlet 17[c] for a suitable temperature regulating fluid is preferably connected in pipe 17 between the desulfurizer 13 and the hydrogenator 21. The temperature of the vapors is preferably adjusted in the temperature regulator 17[a] to about 240° C. In this form of apparatus the valved outlet 26 from the condenser 25 is connected with a trap 27 where the light oils may be obtained in liquid form and drawn off through the valved outlet 28. The uncondensed gases may advantageously pass through pipe 29 to a scrubber or washer 30 then through the valved connecting pipe 31 to a refrigerator 32 then through pipe 33 to a compressor 34 from which the uncondensed portion of the product is returned through valve pipes 35 and 19 to the hydrogenator 21 as hereinabove described in connection with Fig. 2, the condensed portion of the product passing from the compressor 34 may be caught in the trap 36 and drawn off through the valve controlled outlet 37.

The desulfurizing may be placed in any one of several [fol. 1280] locations and may be omitted when the oil is sufficiently free from toxic bodies to have no substantial or objectionable effect on the catalyzer. When water is used in the decomposing tube and an excess is employed this will appear later, on condensation and suitable means should be provided for its removal. The apparatus is preferably run at a slight pressure although a considerable pressure, as several atmospheres may be employed if desired.

The foregoing description of the present system of treatment is not to be construed as a limitation by virtue of any detail herein specified as various deviations therefrom will now be evident to those skilled in this art. For example,

various elements may be eliminated under due circumstances, such as the desulfurizer when the oil is at the start sufficiently free from sulfur poisons. Or various elements may be added to the present system, or hydrogenation of the unsaturated components may take place in the liquid state, instead of in the vapor state as specified; the oil then for example being contacted under pressure with finely-divided catalyzer as hydrogen is caused to pass through or contact with the oil while the catalyzer is maintained well intermingled with the oil by any suitable means.

What I claim is:

1. The system of making a gasolene substitute which comprises passing a kerosene or heavier oil through a heated zone wherein decomposition of the oil takes place, in passing the products of decomposition into a digestion chamber and exposing said vapors to digesting conditions, fractionating to remove the heavy fractions, desulfuring the light fractions and hydrogenating same.

2. The system of making gasolene substitute which comprises passing kerosene material through a heated zone in the presence of heat-conducting and catalytic material, in allowing the decomposed material to itner-react to establish equilibrium by digestion, in fractionating same, in collecting the light oil, removing any toxic traces of sulfur present and in hydrogenating the product.

3. The system of making a gasolene substitute which comprises passing kerosene vapors and the like admixed with the vapors of steam through a long passage way heated to a temperature between 400-600° C. and containing first a quantity of metal material comprising copper and second in series a quantity of metal material comprising nickel, in withdrawing the products of decomposition, passing same into and through a digester of great length in order to establish equilibrium in part, in fractionating in collecting the heavy oil as gas oil and kerosene on the one hand and light volatile oil on the other hand, in removing any toxic traces of sulfur from the light volatile oil, and in combining hydrogen with said light volatile oil.

4. The system of making a gasolene substitute which comprises passing kerosene vapors and the like admixed with

the vapors of steam through a long passage way heated to a temperature between 400-600° C. and containing first a quantity of metal material comprising copper and second a quantity of metal material comprising nickel, in withdrawing the products of decomposition and passing these through a digestion conduit of great length, in fractionating, in collecting the heavy oil as gas oil and kerosene on the one hand and light volatile oil on the other hand, in removing any toxic traces of sulfur from the light volatile oil, and in combining hydrogen with said light volatile oil.

5. The system of making a gasolene substitute which comprises passing oils heavier than gasolene through a heat decomposing zone, in digesting the products of decomposition for a protracted period whereby stable saturated bodies are formed, in fractionating to remove the heavier oils, in collecting the uncondensed vapors of light oils and accompanying gases, in passing same through a desulfurizer to remove traces of toxic bodies, in adjusting the temperature to approximately 240-250° C., in passing the vapors and gases through a mass of nickel material in the presence of hydrogen, in condensing the light volatile oil stabilized by hydrogenation, in collecting the gases and removing therefrom the entrained vapors, in combining the very light oils thus secured or any suitable portion thereof with the aforesaid light oils coming from the condensing apparatus, in submitting some portion at least of said gases to a high temperature, whereby decomposition of hydrocarbons takes place, in freeing the hydrogen thereby secured from objectionable impurities and returning same to the zone of hydrogenation.

6. The system of making a gasolene substitute which comprises passing oils heavier than gasolene through a heat decomposing zone, in stabilizing by digesting the products of decomposition, in fractionating to remove the heavier oils, in collecting the uncondensed vapors of light oils and accompanying gases, in pasing same through a desulfurizer to remove traces of toxic bodies, in adjusting the temperature to approximately 240-250° C., in passing the vapors and gases through a mass of nickel material in the presence of hydrogen, in condensing the light volatile oil stabilized by hydrogenation, in collecting the gases and removing

therefrom the entrained vapors, in combining the very light oils thus secured or any portion thereof with the aforesaid [fol. 1281] light oils coming from the condensing apparatus, in submitting some portion at least of said gases to a high temperature, whereby decomposition of hydrocarbons takes place, in freeing the hydrogen thereby secured from objectionable impurities and returning same to the zone of hydrogenation.

7. The system of making a gasolene substitute which comprises passing oils heavier than gasolene through a heat decomposing zone, in fractionating to remove the heavier oils, in collecting the uncondensed vapors of light oils and accompanying gases, in saturating these in part by digesting causing interaction and formation of more stable products, in passing the vapors and gases through a mass of nickel material in the precence of hydrogen, in condensing the light volatile oil stabilized by hydrogenation, in collecting the gases and removing therefrom the entrained vapors, in combining the very light oils thus secured or any suitable portion thereof with the aforesaid light oils coming from the condensing apparatus, in submitting some portion at least of said gases to a higher temperature, whereby decomposition of hydracarbons takes place, in freeing the hydrogen thereby secured from objectionable impurities and returning same to the zone of hydrogenation.

8. The process of producing gasolene-like material from heavier oil which consists in heating it to the decomposition temperature of the principal constituents thereof, digesting the resulting decomposition products by holding such products without the substantial loss of heat so that they react upon themselves, and hydrogenating the gasolene-like material produced.

9. The process of producing gasolene-like material from heavier oil which consists in heating it to the decomposition temperature of the principal constituents thereof, digesting the resulting decomposition products by holding such products without the substantial loss of heat so that they react upon themselves, and hydrogenating the gasolene-like material produced by subjecting it to the action of hydrogen in

the presence of a catalyzer carried by non-porous material, at an elevated temperature.

10. The process of producing gasolene-like material from heavier oil which consists in heating it to the decomposition temperature of the principal constituents thereof, digesting the resulting decomposition products by holding such products without the substantial loss of heat so that they react upon themselves, and hydrogenating the gasolene-like material produced by subjecting it to the action of hydrogen in the presence of nickel plated upon a vitreous support, at an elevated temperature.

11. The process of producing gasolene-like material from heavier oil which consists in heating it to the decomposition temperature of the principal constituents thereof, digesting the resulting decomposition products, by holding such products without the substantial loss of heat so that they react upon themselves, removing catalyzer poisons from the gasolene-like material produced and hydrogenating such gasolene-like material.

12. The process of producing gasolene-like material from heavier oil which consists in heating it to the decomposition temperature of the principal constituents thereof, digesting the resulting decomposition products, removing catalyzer poisons from the gasolene-like material produced, by the action of spent catalyzer and hydrogenating the thus purified product.

13. A stabilized gasolene-like product comprising digested and hydrogenated volatile petroleum material.

14. A gasolene-like product comprising digested and hydrogenated decomposition products of petroleum oil.

Signed at Montclair in the county of Essex and State of New Jersey this 2nd day of October, A. D. 1913.

Carleton Ellis.

Witnesses: A. A. Wells, F. Carbutt.

4682

[fol. 1282]

PETITIONER'S EXHIBIT 191

E. M. CLARK.

ART OF PRESSURE DISTILLATION

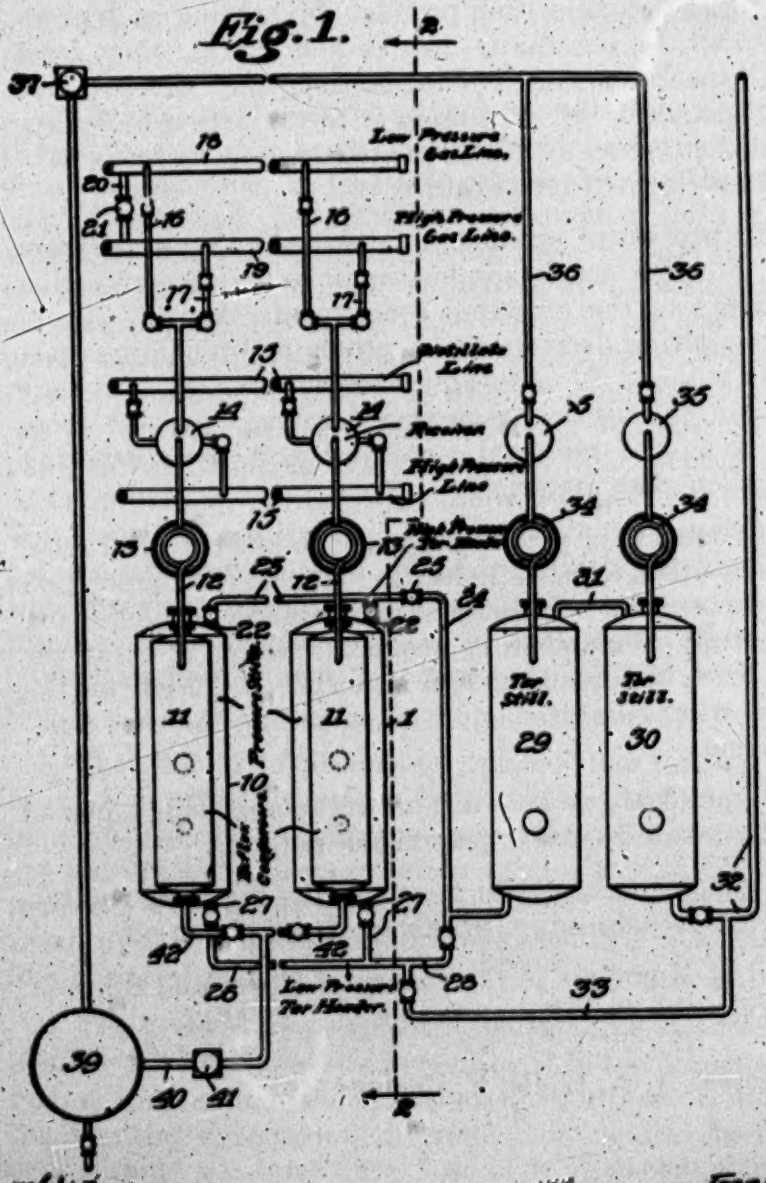
APPLICATION FILED APR. 2 1919

1,410,797.

Patented Mar. 28, 1922.

2 SHEETS—SHEET 1.

Fig. 1.



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PX 191-1

[fol. 1283]

E. M. CLARK.

ART OF PRESSURE DISTILLATION.

APPLICATION FILED APR. 21, 1919.

1,410,797.

Patented Mar. 28, 1922.

2 SHEETS—SHEET 2.

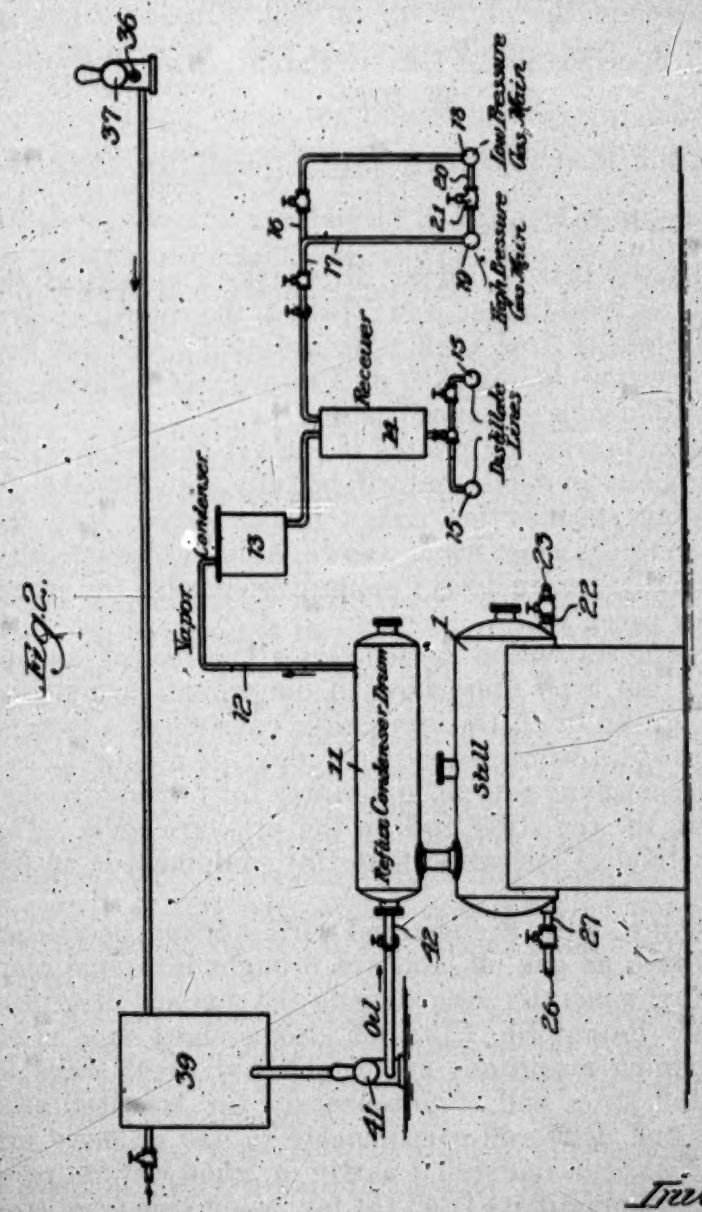

Fig 2.

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PX 191-2

[fol. 1284] United States Patent Office

Edgar M. Clark, of New York, N. Y., Assignor to Standard Oil Company, of New York, N. Y., A Corporation of New Jersey

Art of Pressure Distillation

1,410,797. Specification of Letters Patent. Patented March 28, 1922

Application filed April 21, 1919. Serial No. 291,503

To all whom it may concern:

Be it known that I, Edgar M. Clark, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented a new and useful Improvement in the Art of Pressure Distillation, of which the following is a specification.

The present invention relates to the art of pressure distillation of petroleum oils and will be fully understood from the following specification, taken in connection with the accompanying drawing, which shows in diagrammatic plan view (partially broken away) apparatus suitable for carrying out this invention.

The present invention contemplates the use of an apparatus of the type illustrated in diagrammatic plan on the drawing. In brief, this apparatus consists of a battery of pressure stills connected with an adequate number of tar stills of the continuous type, and means for feeding the distillate from the tar stills back to the pressure stills. The general method of operation with this equipment is as follows:

The pressure stills are charged with a heavy petroleum distillate, such as gas oil, and are brought into operation and operated generally according to the manner described in my Prior Patent No. 1,132,163. Some short time after normal running conditions are established, fresh stock is fed into the stills and simultaneously tar is withdrawn therefrom and delivered continuously to one or more tar stills in which it is redistilled partly or wholly by its residual heat. The distillate from the tar, being free from suspended carbon and dirt, is continuously returned to the pressure stills. By this method of operation a process,

which as heretofore commonly practiced was of a batch or intermittent nature, becomes substantially continuous in character with a resulting increased output of the equipment and reduced fuel and labor costs.

The manner in which this general plan of operation is carried out according to my invention will now be described with reference to the apparatus illustrated by the drawings, in which—

Figure 1 is a plan view, somewhat diagrammatic, showing the apparatus; Figure 2 is a sectional elevation on the line 2—2 of Figure 1.

This apparatus consists of a battery of pressure-stills, the battery being indicated on the drawing by the two end stills designated 1 and 10, respectively. In general, such a battery would consist of six to twenty stills arranged in a row as indicated by the drawing and be at the same horizontal level. Each still will be equipped with its individual reflux fractionating condenser which may, for example, be of the type illustrated in my co-pending application, Serial No. 286,263, executed by me on the 26th day of March, 1919. From these condensers, which are designated 11 in the drawing, the vapor line 12 of each still leads to a water-cooled condenser 13 and thence to a receiving drum for distillate, designated 14. The distillate as collected in this receiving drum may be drawn out by the distillate lines 15 of which there will generally be two as indicated by the drawing. The top of each receiving drum will be connected by branching valved pipes designated, 16 and 17, to low and high-pressure gas mains designated 18 and 19 respectively. A cross-over connection 20 between these gas mains is equipped with a pressure-regulating valve 21. The construction of this part of the apparatus is more fully described and illustrated in my former patent heretofore referred to.

At a point below the normal liquid level in each still, the particular point being determined by the form of still employed, there will be connected a valved high-pressure tar draw-off as indicated at 22 on the drawing. These tar draw-off lines from the several stills will be manifolded to a common high-pressure tar header 23. At the end of the battery this high-pressure tar header will discharge into a low-pressure tar line 24 through a pressure release and control valve 25. A separate low-pressure tar header desig-

nated 26 will also extend along the battery and be provided with valve connections 27 for each still, these low-pressure tar connections being tapped into the lowest point in the still, so that the latter may be completely emptied through them. The low-pressure tar header 26 will communicate with the tar line 24 through a valve connection 28.

The tar line 24 discharges into a continuous tar still 29 arranged preferably at the same horizontal level as the still battery. Where, as will often be the case, the number [fol. 1285] of pressure stills in the battery is so large as to require the use of more than one tar still, I prefer to employ two or more tar stills arranged for continuous operation. Thus, as is shown in the drawing, there is a second tar still 30 beyond the still 29, the second still being connected with the first by an overflow connection 31 of the usual type. From the tar still 30 a line 32 will be carried off through the usual tar coolers and to storage. There may be employed a cross-over connection 33 from the low-pressure tar header 26 to the line 32.

Each tar still will be equipped with its separate condenser 34 and receiver 35. From the receivers distillate lines 36, which may be manifolded, lead to a tar distillate pump 37 which discharges by the line 38 into the feed-stock tank 39. Into the latter there is connected a feed line 40 through a pressure feed pump 41. The feed line will have valved connections, such as those shown at 42, discharging into each still of the battery. Preferably these feed connections will feed the stills through the reflux condensers 11 thereof, as is described in my co-pending application heretofore referred to.

The normal condition of operation in a battery pressure-still, such as that described, will be as follows:

Each still will contain a charge of relatively heavy petroleum oil, such as gas oil, and the stills will all be in communication through their vapor pipes, condensers and receiving drums with the same high-pressure gas main 19. The pressure in this main will be continuously controlled by the regulating valve 21 through which the high-pressure gas escapes to the low-pressure main 18. The operating pressure of the high-pressure main may be, for example, ninety pounds per square inch. Each still will be fired separately at such a rate as to keep its contents at a temperature of about 740° F., under which conditions decom-

position of the oil within the still will proceed at a relatively rapid rate, and the evolved vapors of the lighter products of the decomposition admixed to a considerable extent with the heavier products will pass from the stills into the reflux fractionating condensers 11. In the latter, a separation of the heavier and lighter constituents of the vapors will take place, the heavier constituents being continuously returned to the still, while the lighter ones pass unchanged to the water-cooled condensers 13 and thence to the receiving drums 14. Those portions of the lighter products of the operation which are condensable under the temperature and pressure conditions obtaining will be withdrawn as liquid from the receiving drums, while the incondensable fractions, that is, the fixed gases, will be discharged continuously from the tops of the receiving drums through the open pipe connections 17 to the high-pressure gas main 19.

By virtue of this open communication between all of the stills of the battery afforded by the high-pressure gas main, the entire battery will operate under the same pressure, any variations of pressure incident to irregular operation affecting the entire battery in the same way and at the same time.

Assuming that the battery pressure-still is operating in the normal fashion as described above, the feed-pump 41 will be set in operation and the valves in the feed connections to the individual stills will be opened to such an extent as to supply fresh stock to each still at a rate somewhat greater than the production of distillate within the still. For example, if the stills are producing distillate at the rate of 250 gallons per hour (for each still having a charging capacity of 13,000 gallons), the fresh charge of heavy oil may be continuously fed in at the rate of 460 gallons per hour. Simultaneously all of the stills in the battery will be connected with the high-pressure tar header 23 by opening the individual valves 22. The pressure release and control valve 25 will now be open and regulated so as to maintain the liquid level at the desired point within the stills. Since each still is being fed 210 gallons more per hour than it is producing as distillate, this amount of tar will therefore flow continuously from each still into the tar header 23. Since all of the stills are operating under precisely the same pressure at all times, and since they are

all located on the same level, the liquid level within all of the stills will remain the same, the level for the entire battery being controlled by the setting of the valve 25.

The tar released from the valve 25 into the tar line 24 will be fed continuously to the first tar still 29. In the latter, its residual or super heat (the tar still operating at atmospheric pressure) will be sufficient to vaporize a considerable percentage of its volume, the vapors being collected as distilled in the receiver 35. If desired, the still 29 may be operated entirely by residual or super heat in this manner, no additional heat being applied to it. From the still 29 the tar (which may be reduced in volume to a considerable extent) may overflow into the still 30 which will be fired to effect a further reduction in volume and production of distillate. For example, the tar received from the pressure stills and fed by the tar stills may have a gravity of 27° Baumé and by the tar stills this tar may be reduced to 14° Baumé, which is accomplished by taking off approximately 55 per cent of its volume as distillate. I prefer to aid the distillation in both tar stills by the use of submerged steam jets therein, the distillation with steam giving a better product, particularly a better residual [fol. 1286] product. The mixed distillate taken off the two tar stills may have a gravity of 31.5° Baumé. These mixed distillates through the manifold connections shown and by the pump 37 will be continuously delivered to the feed tank 39 in which they will usually be mixed with other stock. The contents of the feed tank, including a considerable percentage (for example 27½%) of the returned distillate from the tar of the pressure-stills, will be continuously fed into these stills in the manner above described.

Should it be necessary to discontinue the operation of any particular still in the battery, the latter is disconnected from the high-pressure header 19 by shutting off the valve in the connection 17. Simultaneously, the connection 22 to the high-pressure tar line will be closed and the feed to that still stopped. The contents of the still may then be evacuated through the low-pressure tar line 26 which may discharge into the tar line 24 and thence to the tar re-running stills or by the cross-over 33 directly into the residual line from the tar stills.

I have found that by continuously withddrawing a portion of the material under treatment from the pressure-

stills and continuously feeding a sufficient quantity of fresh stock to maintain a constant level therein, it is possible to prolong the continuous period of operation of the stills to such an extent that the output of light distillate from the equipment is substantially increased. I prefer to operate by charging each still into the battery initially and running off by the batch method, that is, without either feeding or withdrawing tar, approximately twenty per cent of the contents of the still before putting the still into communication with the high-pressure tar header and beginning the feed. I have found it easily possible to operate stills in this manner continuously for a week at a time without interrupting the pressure process for the purpose of cleaning the stills.

While I have in the foregoing described in considerable detail the preferred process according to my invention, together with a lay-out of apparatus suitable for this particular process, it will be understood that this is illustrative only, and that my invention is not limited to the details of procedure or apparatus described, except in so far as such limitations form a part of the accompanying claims, in which it is my intention to claim all novelty inherent in the invention as broadly as is permissible in view of the prior art.

What I claim is—

1. The improvement in the art of pressure distillation of petroleum oils for the purpose of producing lighter products by pyrogenesis, which consists in maintaining a considerable body of said oil under cracking conditions of temperature and pressure, continuously withdrawing oil from the said body, releasing the pressure from the withdrawn oil while the latter is in a heated condition, whereby its lighter fractions will distill off, collecting such lighter fractions and returning them to the oil body for further cracking therein.

2. The improvement in the art of pressure distillation of petroleum oil which consists in carrying on the distilling operation simultaneously in a plurality of separate stills, all at substantially the same horizontal level, maintaining free communication between the vapor spaces of all of said stills, maintaining separate free communication be-

tween the liquid bodies of all of said stills, withdrawing liquid from the communication means, whereby liquid is withdrawn from all stills, and simultaneously feeding the said stills separately and independently.

3. A continuous process of distilling petroleum oil under pressure which consists in operating simultaneously a plurality of separate pressure stills, all at the same horizontal level, separately condensing and collecting*ing* the distillate of each still, maintaining a uniform pressure in all of the stills by permitting a free inter-flow of uncondensed products of distillation between stills, withdrawing liquid from all stills simultaneously and through a common draw-off line, distilling the withdrawn liquid, and feeding the stills separately with the distillate of the withdrawn liquid supplemented by a sufficient quantity of fresh oil to maintain a constant level in each still.

4. The distillatory apparatus comprising a plurality of stills, vapor apparatus connected to each of said stills, each vapor apparatus comprising a condenser system, a gas main communicating with the vapor apparatus of each still, a tar line communicating with each still, a tar still into which the tar line discharges, means for feeding stock into the vapor apparatus of each still, and means connecting the condenser of said tar still to said feeding means.

Edgar M. Clark.

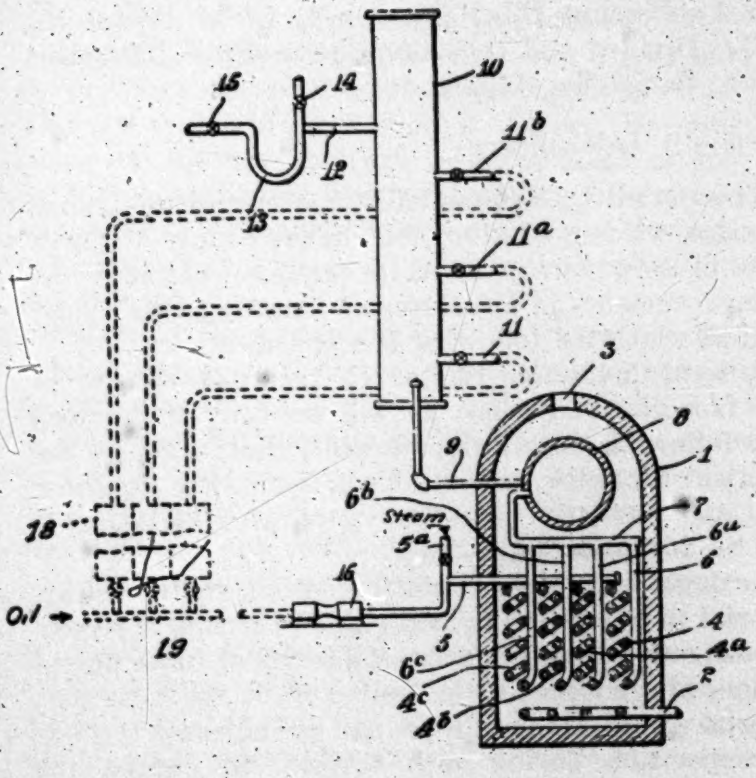
[fol. 1287] PETITIONER'S EXHIBIT 192.

C. ELLIS.

PROCESS OF CRACKING OILS UNDER PRESSURE.

APPLICATION FILED NOV. 26, 1920

1,415,232. Patented May 9, 1922.



Attest.

Inventor:

[fol. 1288] United States Patent Office

Carleton Ellis, of Montclair, New Jersey, Assignor by Mesne Assignments, to Standard Oil Company, a Corporation of New Jersey

Process of Cracking Oils Under Pressure

1,415,232. Specification of Letters Patent. Patented May 9, 1922

Original Application Filed October 4, 1913. Serial No. 793,377. Divided and this Application Filed November 26, 1920. Serial No. 426,501

To all whom it may concern:

Be it known that I, Carleton Ellis, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Processes of Cracking Oils Under Pressure, of which the following is a specification.

The present invention relates to the manufacture of gasolene from heavier oils. It will be fully understood from the following description thereof, illustrated by the accompanying drawing, which shows somewhat diagrammatically and partially in section apparatus suitable for carrying the invention into effect.

In accordance with the present invention, the hydrocarbon material to be treated is first passed through a decomposer, which may suitably consist of a series of tubes placed in a furnace and adapted to be heated while the hydrocarbon material passes through them and is subjected to thermal decomposition during such travel. Of course, the length of the tubes, the velocity of travel of the hydrocarbon material and the temperature of the surrounding heating gases may be proportioned with respect to each other. A quantity of steam may be introduced into the decomposer along with the oil or oil vapors, the quantity of steam being such as to provide water up to 20-50%, more or less, based on the nature of the oil employed. After the hydrocarbon materials have passed through the decomposing tubes to which a strong heat is applied externally to bring them to decomposing temperature of 400

to 600° C. or so, they pass to a vessel or container well insulated to prevent loss of heat, in which container the heated hydrocarbon materials undergo further reaction with establishment of certain conditions which could not be secured satisfactorily in the decomposing tubes. From the vessel or container the products may pass into a dephlegmator or fractionating column, which may be suitably arranged to yield as fractions a gas oil and unconverted kerosene, especially if the latter is employed as the raw material. Either or both of these products may be returned to the decomposing tubes if desired.

The lighter oils or volatile spirits are condensed either in the dephlegmator or in a subsequent condenser (not shown). The condensed product may, if desired, be redistilled or refined by means of sulfuric acid and alkali or subjected to any other method of treatment, although in general this is unnecessary when the products are passed through a hydrogenating device, such as is shown in the application of which this is a division.

Referring more particularly to the drawings, the numeral 1 indicates a furnace structure containing a battery of heating tubes as shown at 4, 4^a, 4^b and 4^c. These tubes consist of pipes set horizontally or practically so, connected end to end in such manner as to form a continuous passage from the upper horizontal tubes to the lower ones. They are heated by any suitable means, for example, by fuel gas supplied through the pipes 2. A stack or chimney opening 3 for removal of the spent gases or products of combustion, is provided. A feed pipe 5 serves for the introduction of oil, oil vapors, oil and water, steam and oil, the steam being supplied, for example through 5^a or the vapors of steam and oil. These pass downwardly through the several series of heating pipes and then by risers 6, 6^a, 6^b and 6^c, are taken to the manifold 7 which communicates with the drum 8, which, as clearly indicated in the drawing, is of much greater diameter than the decomposing or heating tubes. The drum is preferably of considerable length with reference to its diameter and has an inlet for hydrocarbon material at one end and its outlet 9 preferably at the other end. The products of combustion from the heaters below the decomposing tubes pass up and around the drum and in some cases may add heat to it and in other cases serve

more as an insulating blanket of heated air to prevent any substantial drop of temperature in the drum 8. The hydrocarbon material travels slowly through the drum so that further conversion may take place therein.

The outlet pipe 9 leads to a dephlegmator 10 which may be a column apparatus of the type adapted to make a thoroughly sharp separation of close boiling fractions, which may be withdrawn at 11, 11^a and 11^b. These pipes may suitably lead these fractions to receivers 18, from [fol. 1289] which suitable connections may lead to the supply manifold 19 for oil or hydrocarbon material. A pipe 12 carries out the light converted products through valve 15. Gases are withdrawn through a valve 14. A trap 13 enables gases to be collected at that point.

When water is used in the decomposing tubes and an excess is employed, this will appear later, on condensation and suitable means should be provided for its removal. The apparatus may be run at a slight pressure or a considerable pressure, as several atmospheres may be employed if desired. This application is a division of my prior application Serial No. 793,377, filed October 4, 1913.

What I claim is:

1. The process of making a gasolene substitute which comprises passing a kerosene or heavier oil through a heated zone wherein the oil is brought to a decomposing temperature in a single passage, and passing the products at a slower rate through an enlarged passageway without increasing their temperature, and without permitting the temperature to drop below a decomposing temperature and maintaining superatmospheric pressure upon the oil in its passage through the heated zone and the enlarged passageway.

2. The process of making a gasolene substitute which comprises passing hydrocarbon material through a long passageway subjected to a high external temperature whereby the hydrocarbon material is brought to a decomposing temperature and substantial conversion thereof is effected passing the products of decomposition at a slower rate through an enlarged passageway in which their temperature is substantially maintained without rise and wherein further substantial change in the oil occurs, and

maintaining superatmospheric pressure in both said passageways.

3. The method of making a gasolene substitute which comprises passing hydrocarbon material admixed with steam through a long passageway subjected to a high external temperature, whereby the hydrocarbon material is brought to a decomposing temperature, passing the products of decomposition through an enlarged container in which further substantial conversion of the hydrocarbon products is effected without increasing their temperature and removing the products formed in said container through a single outlet.

4. The method of making a gasolene substitute which comprises passing hydrocarbon material once through an elongated passageway subjected to a high external temperature, whereby it is brought to a decomposing temperature, passing the hydrocarbon material from said passageway into an enlarged chamber in which the temperature of the products does not rise, a decomposing temperature being maintained therein, whereby further conversion of the hydrocarbon material is effected, and maintaining superatmospheric pressure throughout the system.

5. The method of making a gasolene substitute which comprises passing hydrocarbon material once through an elongated passageway subjected to a high external temperature, whereby it is brought to a decomposing temperature, passing the hydrocarbon material from said passageway into an enlarged chamber in which the temperature of the products does not rise, a decomposing temperature being maintained therein, whereby further conversion of the hydrocarbon material is effected, removing the decomposition products from the enlarged chamber through a single outlet and maintaining superatmospheric pressure throughout the system.

6. The process of making a gasolene substitute which comprises passing hydrocarbon material heavier than gasolene through a long passageway, being subjected therein to a temperature of 400 to 600° C., and thereby brought to a decomposing temperature passing the products of decomposition through an enlarged passageway subjected to a

lower external temperature whereby no rise in temperature takes place therein, a decomposing temperature being maintained removing the products of d-ige-s-tion from said enlarged passageway and maintaining superatmospheric pressure in said passage.

7. The process of making a gasolene substitute which comprises passing hydrocarbon material heavier than gasolene through a long passageway, being subjected therein to a temperature of 400 to 600° C., and thereby brought to a decomposing temperature passing the products of decomposition through an enlarged passageway subjected to a lower external temperature whereby no rise in temperature takes place therein, a decomposing temperature being maintained removing the products thereof from said enlarged passageway through a single outlet and maintaining pressure throughout the passageways.

8. The process of making a gasolene substitute which comprises passing hydrocarbon material heavier than gasolene through a long passageway subjected to a high external temperature, thereby bringing it to a decomposing temperature withdrawing and holding the products of decomposition at a decomposing temperature without increasing their temperature, thereby effecting further substantial conversion thereof, superatmospheric pressure being maintained thereupon, separating the products thereof into oils heavier than gasolene on one hand and volatile [fol. 1290] products on the other hand, and returning the heavier oils to the highly heated passageway.

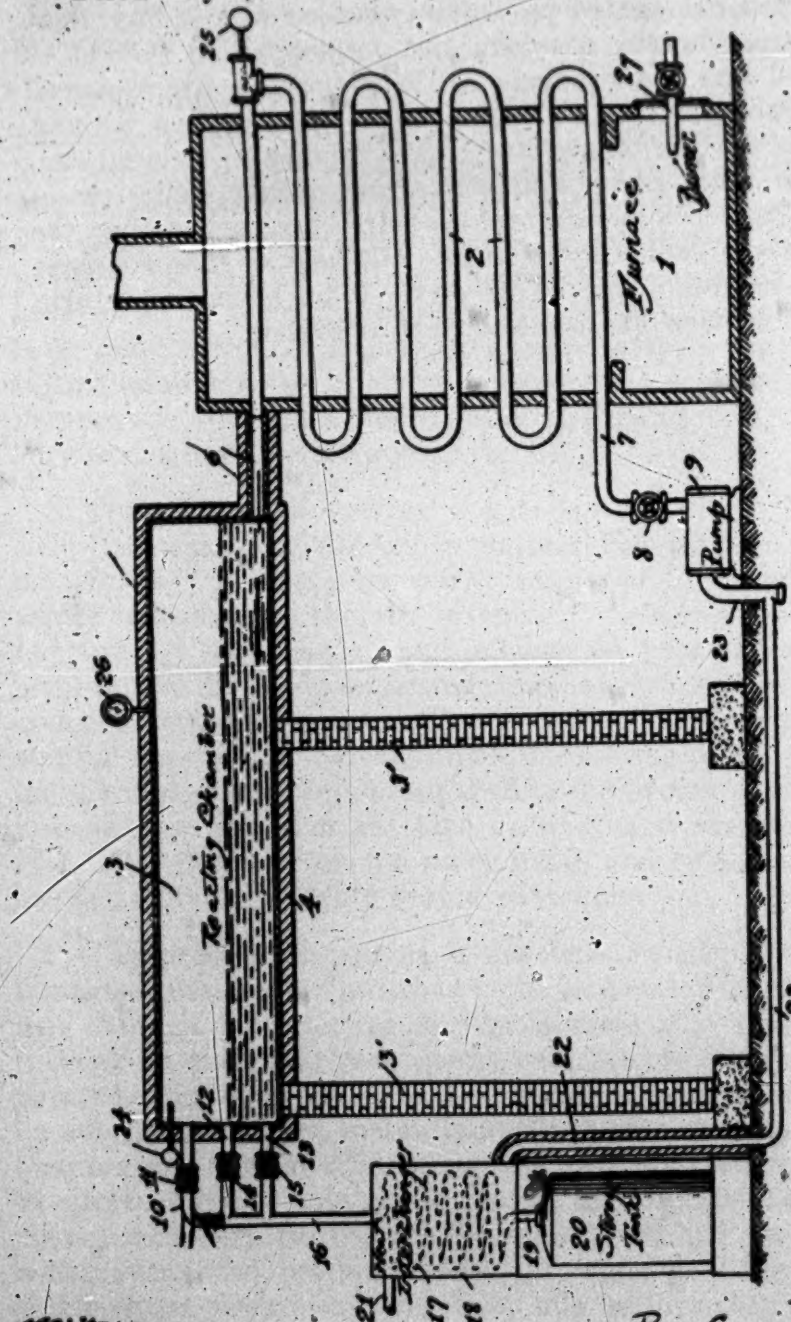
9. The process of making a gasolene substitute which comprises passing hydrocarbon material heavier than gasolene through a converting system wherein it passes once through an elongated passageway subjected to a high temperature and the products of decomposition are passed into an enlarged chamber, maintaining them at a decomposing temperature therein without increasing their temperature to effect a further substantial change therein, maintaining superatmospheric pressure in the passageway and chamber, withdrawing the products from the chamber through a single outlet, separating therefrom oils heavier than gasolene and returning said oil to the converting system.

10. The process of making a gasolene substitute which comprises passing hydrocarbon material heavier than gasolene through a converting system wherein it passes once through an elongated passageway subjected to a high temperature, whereby a substantial decomposition thereof is effected and the products of decomposition are removed and maintained at a decomposition temperature without increasing their temperature, until further substantial conversion takes place said converting system being maintained under superatmospheric pressure, separating the products of said conversion into oils heavier than gasolene on one hand and volatile oils on the other hand, and returning the heavier oils to the converting system.

Carleton Ellis.

[fol. 1291] PETITIONER'S EXHIBIT -193

R. Cross. Process of Treating Petroleum Oil. Application Filed May 2, 1921. 1,423,500. Patented July 18, 1922



[fol. 1292] United States Patent Office

Roy Cross, of Kansas City, Missouri, Assignor to Gasoline Products Company, Inc., of New York, N. Y., a Corporation of New York

Process of Treating Petroleum Oil

1,423,500. Specification of Letters Patent. Patented July 18, 1922

Continuation of Application Serial No. 211,407. Filed January 11, 1918. This Application Filed May 2, 1921. Serial No. 466,119

To all whom it may concern:

Be it known that I, Roy Cross, a citizen of the United States, residing in the city of Kansas City, county of Jackson, and State of Missouri, have invented certain new and useful Improvements in Processes of Treating Petroleum Oil, of which the following is a specification.

This invention relates to improvements in process for treating petroleum oils and more particularly refers to a process for making light hydrocarbon bodies, such as gasolene, naphtha and the like in which there is a conversion of hydrocarbons having a relatively high specific gravity to those having a lower specific gravity.

This application is a continuation of an original application filed by me January 11th, 1918, Serial No. 211,407.

Among the salient objects of the invention are to provide a process in which the heat, which is transmitted to the oil in the heating zone, is conserved and maintained in the body of the oil until such time as the oil has had an opportunity to react or attain a substantial equilibrium under the cracking temperature and pressure to which it is subjected; to provide a process in which the decomposition or reaction of the oil in the reacting zone produces an increased pressure, which assists in raising the boiling point of the oil and thereby promoting the decomposition of the oil; to provide a process that can be operated continuously and one that affords a more complete conversion of the oil body in that the temterature is not materially decreased in the reacting zone by such endothermic reactions as vaporization and radiation; to provide a process in which certain of the gases produced

by the process, having a critical temperature below the cracking temperature of the charging stock, are intermittently or continuously removed from the reacting zone so as to prevent an excessive or unnecessary pressure in said reacting zone; to provide a process which is economical of operation in that the heat is more or less retained in the oil body during decomposition of the oil itself; to provide a process in which the heat from the gases and oils discharged from the reacting zone is utilized to preheat the fresh charging stock, which action also serves to cool such oil and gases and, in general, to provide an improved process of the character referred to.

The accompanying drawing shows a view partly in side elevation and partly in vertical section of an apparatus for carrying out the invention.

In the present invention the oil to be treated is fed continuously through a heating zone as, for example, through a continuous coil of pipe seated in a suitable furnace and there heated to the desired reacting temperature. The oil then in substantially liquid phase is passed to a reacting zone which may take the form of an enlarged chamber which is insulated from radiation and maintained under the same pressure as the oil in the heating zone. This pressure is maintained substantially uniform in both the coil tube and the reacting chamber 3 by reason of the accumulated gases in the upper part of the reacting chamber. The oil having been heated to a cracking temperature in the heating zone continues to react while in the reacting zone, such reaction taking place substantially in the liquid phase due to the high pressure maintained, although there will be formed some gases which may be such as methane, ethane, pentane, hexane, and other substances having a critical temperature below the cracking temperature of the oil under treatment. In other words, certain gases as formed by the cracking of the oil and should be removed from the system to prevent undue rise of pressure. There may also be entrained with these gases some small amount of condensable vapors. The bulk of the oil will be removed after the cracking reaction in the form of liquid or in a liquid phase.

This process is in no wise to be confused with the many distillation processes for cracking oil in which the light hydrocarbons are removed from the cracking zone in the form of vapors.

In the cracking of various kinds of oil, the pressure and temperature used will vary. For example, in the cracking

of a mid-continent gas oil a pressure of 750 pounds per square inch has been found advantageous with an oil temperature of 700-800 degrees F.

Referring to the drawings—1 designates a furnace in which are mounted the heating tubes 2 through which the oil [fol. 1293] is passed. These tubes 2 may take the form of a continuous coil of four-inch pipe and may for example, be composed of, say, sixty tubes each twenty feet long. From the heating tubes the oil passes to the reacting chamber 3, which may take the form of a horizontal shell suitably supported as shown at 3' and insulated as shown at 4. This shell may take the form of a horizontal cylinder forty feet long and thirty inches in diameter. The apparatus should be capable of withstanding the desired pressure as, for example 750-100 pounds, if so high a pressure is used. The oil passes in a substantially liquid condition through the insulated conduit 6 from the coil 2 to the chamber 3. Oil is supplied to the coil 2 through the feed line 7 having control valve 8 connected to the feed pump 9. At one end the reacting chamber 3 is provided with an incondensable gas outlet 10 controlled by throttle valve 11 and with liquid drawoff pipes 12 and 13 controlled by throttle valves 14 and 15 respectively. The treated oil containing a large quantity of gasolene and other low boiling point products may be given a distillation treatment, if desired, after which treatment the light oils are separated from the heavy residuum and precipitated carbon and the purified light oils such as fuel oil may be introduced with fresh oil to the system for treatment. The gases accumulating in the reacting chamber may be removed continuously or intermittently, it being necessary, however, in each instance that sufficient gases be retained with the upper part of said reacting chamber to exert a pressure which will serve to cause the oil to reassume its equilibrium. It will likewise be understood that while the gases that have the critical temperature below the boiling point of the main body of oil, largely consist of incondensable gases, although of course certain other gases of the oil which are condensable may mix therewith. The various pipes 10, 12 and 13 connect to a manifold pipe 16 leading to the coil 17 of a heat interchanger 18. The lower end of the coil is connected by pipe 19 to suitable receiver or storage tank 20. Raw oil is supplied to the pump 9 through the line 21 leading to any suitable source of charging stock. The raw

oil is then passed through the heat interchanger 18 where it is preheated by the hot oil and gases passing through the coil 17 and thence delivered by insulated line 22 to the inlet pipe 23 of the charging pump 9. Suitable thermometers 24, 25 and pressure gauge 26 may be provided as well as the burner 27 for the furnace. It will be appreciated that the oil after being subjected to the cracking temperature in the coil 2 is transferred to the reacting chamber 3, which as before stated, is insulated, and in this chamber the oil is subjected to a pressure exerted thereon to permit the same to reassume an equilibrium.

For example, Kansas gas oil as it passes through through the heating coil may be heated to a temperature of, say, 750 degrees F. more or less and the pressure gradually raised in the heating coil and reacting chamber to, say 750 pounds per square inch. When this oil while at the temperature above defined is maintained in the reacting chamber under a pressure of 750 pounds per square inch by means of certain gases evolved from the oil no substantial vaporization of the heated oil takes place, the bulk of the oil reacting or cracking in a liquid phase, in which condition it is withdrawn as treated oil from the reacting chamber. The small quantity of the evolved gases which have a critical temperature below 750° F. maintain the high pressure on the reacting oil in its liquid phase and are discharged with the treated oil in such quantities as to always maintain a pressure in the reacting chamber sufficient to prevent vaporization of the bulk of the oil. It is apparent that if a high pressure is not maintained in the reacting chamber the bulk of the oil heated to this cracking temperature would vaporize, as commonly occurs in all distillation processes that must not be confused with this process which utilizes pressures always sufficiently high to prevent substantial vaporization of the oil. The level of the oil in the reacting chamber may be maintained to about the height of the pipe 12 and the pressure regulated by the withdrawal of the gases having a critical temperature below that of the cracking temperature. The oil is fed continuously through the system and about 30% of the oil will be converted into gasolene, more or less depending on the character of the raw oil being treated.

In an apparatus of the character referred to, the oil may be satisfactorily cracked to the extent indicated by remaining in the apparatus not to exceed, say, twenty minutes from

the time it enters the heating coil until it leaves the reacting chamber. It is to be understood that the process is a continuous one and I wish to emphasize that the bulk of the gasolene and hydrocarbons formed at all times remains in liquid phase by reason of the conditions under which it is treated and substantially the bulk of the light hydrocarbons formed are removed from the system in liquid phase. It is, of course, to be understood that gases are formed which should be removed from the system, as stated, and also that some small amount of gasolene may either be entrained out with the gases or removed as vapor but nevertheless such vaporization is to be prevented as far as possible and is a rather incidental and inconsequential result of the operation of the process.

[fol. 1294] It is well known in the art that in ordinary distillation processes the vaporization and reflux condensation which takes place in such processes results in a very large heat loss which is eliminated in the present process.

I claim as my invention:

1. A continuous process of treating oil under pressure without substantial distillation consisting in passing oil in a relatively small stream through a heating zone where it is heated to a cracking temperature, in passing the oil in a substantially liquid phase while at a cracking temperature to an enlarged insulated reacting chamber located outside of the heating zone where further cracking takes place in maintaining both the insulated reacting chamber and the heating zone under pressure of evolved gases of the oil that have a critical temperature below the cracking temperature, of the bulk of the oil said pressure being sufficient to prevent substantial vaporization of the oil, and in continuously removing said gases and the bulk of the treated oil in liquid phase from said reacting chamber.

2. A continuous process of treating oils under pressure without substantial distillation, consisting in passing the oil in a relatviely small stream through a heating zone where the oil is heated to a cracking temperature, in discharging the oil from the heating zone in a substantially liquid phase and at a cracking temperature to an enlarged insulated reacting chamber located outside of the heating zone where further cracking takes place, maintaining the

oil in both the enlarged insulated reacting chamber and the heating zone under pressuer of evolved gases of the oil having a critical temperature below the cracking temperature of the bulk of the oil, said pressure being always sufficient to prevent any substantial vaporization of the oil, and in continuously removing the bulk of the oil in liquid phase and said pressure gases from said reacting chamber.

3. A continuous process of treating oils under pressure without substantial distillation consisting in passing the oil in a relatively small stream through a heating zone where the oil is heated to a cracking temperature, in transferring the oil while at a cracking temperature and in a substantially liquid phase from the heating zone to an enlarged insulated reacting chamber located outside of the heating zone, in maintaining the oil in the heating zone, and while in the enlarged insulated reacting chamber under pressure of evolved gases of the oil, said pressure being sufficient to prevent any substantial vaporization of the bulk of the oil, and in continuously removing treated oil and gases from the reacting chamber without distillation of said oil.

4. A continuous process for treating oils under pressure without distillation conssisting in passing the oil in a relatively small stream through a heating zone where the oil is heated to a cracking temperature, in transferring the oil while at a cracking temperature and in a substantially liquid phase from the heating zone to an enlarged insulated reacting chamber located outside of the heating zone, in maintaining the oil in the heating zone, and while in the enlarged insulated reacting chamber under a substantially uniform pressure of evolved gases of the oil, said pressure being sufficient to prevent any substantial vaporization of the bulk of the oil, and in continuously removing treated oil and gases from the reacting chamber without returning said oil to the heating zone for retreatment.

5. A process of cracking petroleum oil without substantial distillation, which consists in passing the oil in a relatively small stream through a heating zone to be heated to a cracking temperature and thence to an enlarged insulated reacting chamber while the oil is at a cracking temperature, in maintaining the oil under pressure of

evolved gases while in the heating zone and the enlarged reacting chamber, which pressure is sufficient to prevent a substantial vaporization of the bulk of the oil in the heating zone and the reacting chamber during conversion of the heavier hydrocarbons into increased quantities of lighter hydrocarbons, and in discharging from the enlarged insulated reacting chamber gases and oil without again passing said discharged oil through the heating zone.

6. A process of cracking oil without substantial distillation, consisting in passing the oil in a relatively small stream through a heating zone to be heated to a cracking temperature, and thence to an enlarged insulated reacting chamber, in maintaining the oil in the heating zone and in the enlarged reacting chamber under a pressure of the evolved gases of the oil sufficient to prevent any substantial vaporization of the oil during conversion of the heavier hydrocarbons into increased quantities of lighter hydrocarbons while in the heating zone and the enlarged reacting chamber, and in discharging oil and gases from the enlarged insulating reacting chamber without again introducing the discharged oil to the heating zone.

7. A process of cracking oil without substan-ial distillation, comprising continuously passing oil in a small stream through a heating zone to be heated to a cracking temperature and then to an enlarged insulated reacting chamber, in subjecting the oil while in the heating zone and in the enlarged insulated reacting chamber to a pressure of evolved gases of the oil having critical temperature below [fol. 1295] the cracking temperature, said pressure being sufficient to prevent substantial vaporization of the oil, in removing treated oils and gases from the enlarged insulated reacting chamber, and in collecting the treated oils without again passing said oils through the heating zone.

8. A continuous process of treating petroleum oils without substantial distillation, consisting in passing the oils in a relatively small stream through a heating zone and raising the same to a cracking temperature, directing the oil therefrom to a relatively large insulated reacting chamber and there maintaining the oil under sufficient pressure

of evolved gases of the oil having a critical temperature below the cracking temperature of the bulk of the oil to prevent vaporization of the cracked hydrocarbons, introducing additional fresh oil to the heating zone, and drawing off the cracked liquid oil from the insulated reacting chamber without recirculation of the same through the heating zone while maintaining the temperature and pressure condition substantially uniform.

9. A continuous process of treating petroleum oil without substantial distillation consisting in passing the oil in a relatively small stream through a heating zone where it is raised to a conversion temperature, in introducing the oil to an enlarged insulated reacting zone and there maintaining the oil under pressure of the evolved gases of the oil to prevent vaporization of the heated hydrocarbons, in continuously withdrawing from the enlarged reacting zone sufficient cracked liquid oil and gases to maintain a constant level therein and uniform temperatures and pressures on the system and simultaneously introducing regulated quantities of fresh oil to the heating zone.

10. A continuous process of treating petroleum oil without substantial distillation, consisting in passing the oil in a relatively small stream through a heating zone where it is raised to a cracking temperature under a substantial pressure, then passing the oil to an enlarged insulated reacting zone and there permitting it to collect in a pool while maintaining the oil under pressure of the evolved gases of the oil having a critical temperature below the cracking temperature to prevent vaporization of the hydrocarbons, introducing fresh oil to the heating zone and drawing off cracked oil from the insulated reacting zone while maintaining the temperature and pressures through the system relatively constant.

11. A process of converting heavy petroleum hydrocarbons of substantially the same series without substantial distillation, consisting in bringing the hydrocarbons to a cracking temperature in a heating zone during the continuous passage of the hydrocarbons in a comparatively small stream through said zone, then passing the oil to an enlarged insulated reacting zone where no heat is applied, and

in maintaining it in a relatively greater body in said reacting zone, the oil in both zones being subjected to pressure of the evolved gases of the oil having a critical temperature below the cracking temperature of the main body of oil, by means of which pressure substantial vaporization of the oil in both the heating and reacting zones is prevented during a conversion of the hydrocarbons, in removing treated hydrocarbons and gases from the enlarged insulated reacting chamber without returning said hydrocarbons to the heating zone for retreatment.

12. A process of converting heavy hydrocarbons into lighter hydrocarbons without substantial distillation, comprising passing oil in a small stream continuously through a heating zone to be heated to a cracking temperature, in then discharging the oil into an enlarged insulated reacting chamber wherein a substantial quantity of the heated oil accumulates, in maintaining the oil while passing through the heating zone and when in the enlarged insulated reacting chamber under pressure of evolved gases of said oil, said pressure being sufficient to prevent substantial vaporization of the bulk of the oil that is at a temperature above the cracking temperature, in withdrawing from the enlarged reacting chamber treated oil and pressure gases, and in collecting the treated oil without returning said oil to the heating zone for retreatment.

13. A process of converting petroleum hydrocarbons without substantial distillation consisting in directing the oil in comparatively small streams through the heating zone and raising it to a conversion temperature, passing the oil to an enlarged insulated reacting zone and there collecting it in a relatively greater body, permitting the oil to reassume an equilibrium therein by maintaining sufficient pressure upon the oil by evolved gases of the oil having a critical temperature below the cracking temperature of the main body of the oil to prevent any substantial vaporization, and in drawing off oil and a portion of the pressure gases from the enlarged reacting chamber without retreatment of said withdrawn oil.

14. A process of converting petroleum hydrocarbons without substantial distillation consisting in directing the

oil in comparatively small streams through the heating zone and raising it to a conversion temperature, passing the oil to an enlarged insulated reacting zone and there collecting it in a relatively greater body, permitting the oil to reassume an equilibrium therein without the addition of heat to the reacting chamber by maintaining sufficient pres- [fol. 1296] sure thereon by evolved gases of the oil having a critical temperature below the cracking temperature of the bulk of the oil to prevent any substantial vaporization, withdrawing the oil from the reacting chamber without retreatment thereof in the heating zone, and adding fresh untreated oil to the heating zone.

15. The process of continuously treating hydrocarbon oils without substantial distillation, which consists in introducing oil to a heating zone where the oil is heated in a relatively small stream to a cracking temperature, and in thence discharging the same to an enlarged insulated reacting chamber, in maintaining the oil under pressure of evolved gases while in the heating zone, and the enlarged insulated reacting chamber, which pressure is sufficient to prevent a substantial vaporization of the bulk of the heated oil in the heating zone and the reacting chamber during the conversion thereof, and in withdrawing treated oil and some of the pressure gases from the enlarged insulated reacting chamber, without again returning said withdrawn oil to the heating zone for retreatment.

Roy Cross.

[fol. 1297]

PETITIONER'S EXHIBIT 194

J. H. ADAMS.

PROCESS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED DEC. 5, 1917.

1,433,519. Patented Oct. 24, 1922.

4 SHEETS—SHEET 1.

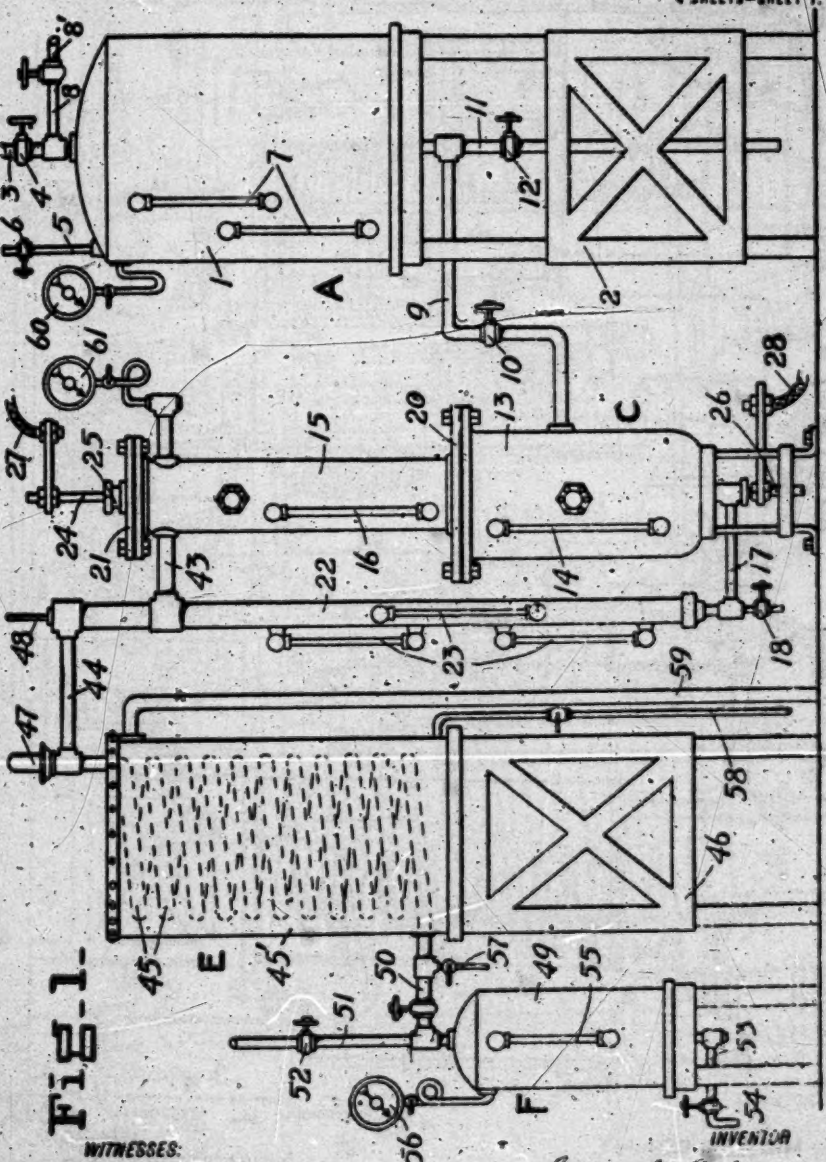


Fig. 1.

WITNESSES:

Austin Adams

Joel Sedgwick

INVENTOR

Joseph H. Adams.

PX 194-1

4710

[fol. 1298]

J. H. ADAMS.

PROCESS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED DEC. 5, 1917.

1,433,519. Patented Oct. 24, 1922.

4 SHEETS—SHEET 2.

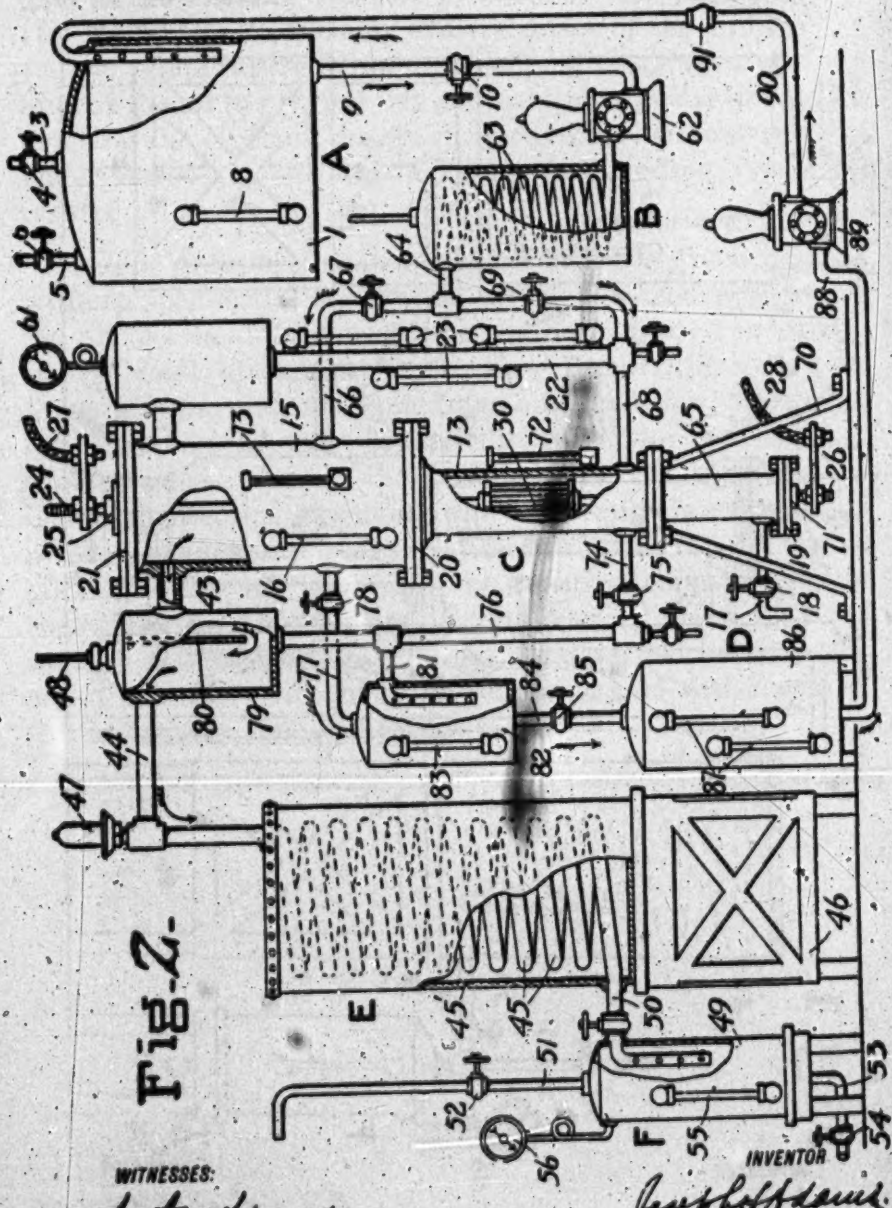


Fig. 2.

WITNESSES:

Austin Adams

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Px 194-2

[fol. 1299]

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PROCESS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED DEC. 5, 1917.

1,433,519. Patented Oct. 24, 1922.

4 SHEETS—SHEET 3.

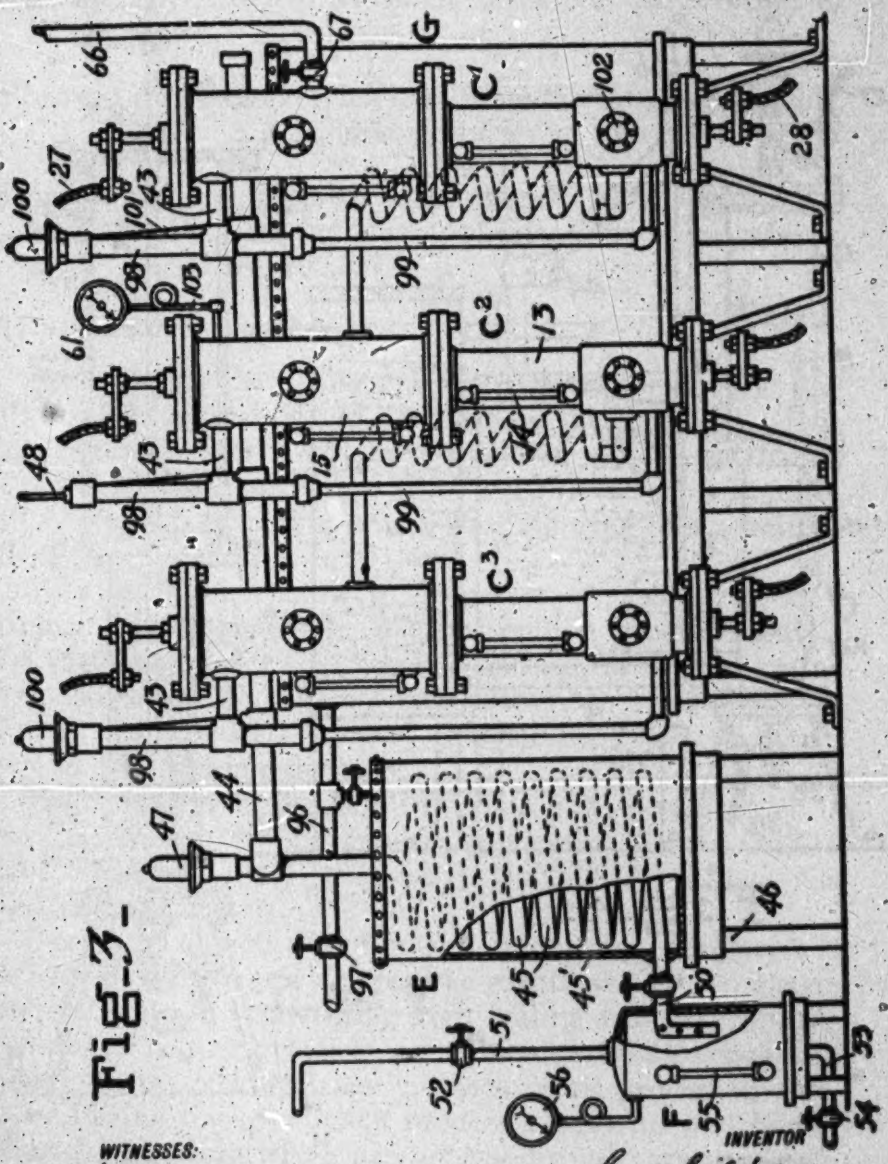

Fig. 3.

WITNESSES:

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PX 194-3

4712

[fol. 1300]

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PROCESS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS.

APPLICATION FILED DEC. 9, 1917

1,433,519. Patented Oct. 24, 1922

4 SHEETS—SHEET 4.

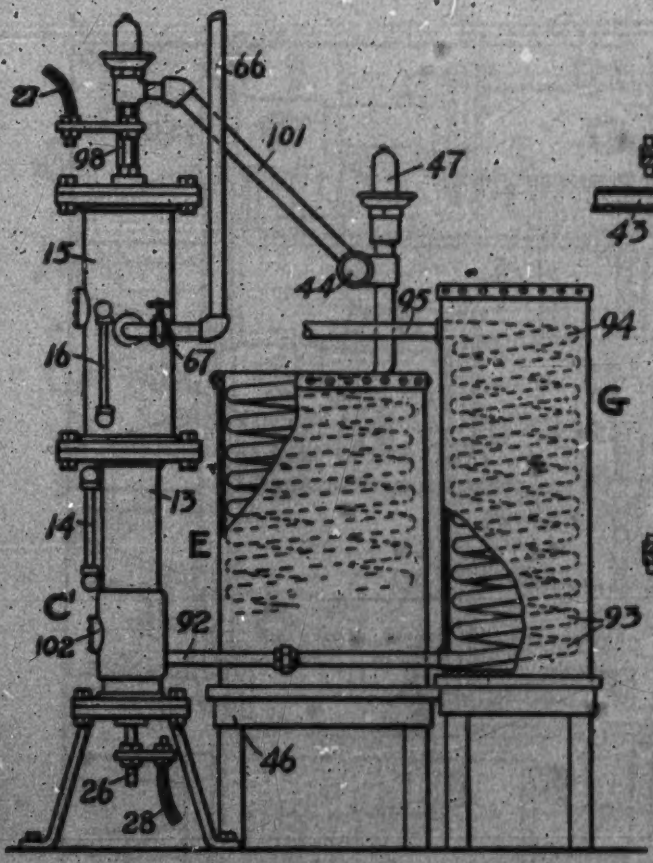

Fig. 4.

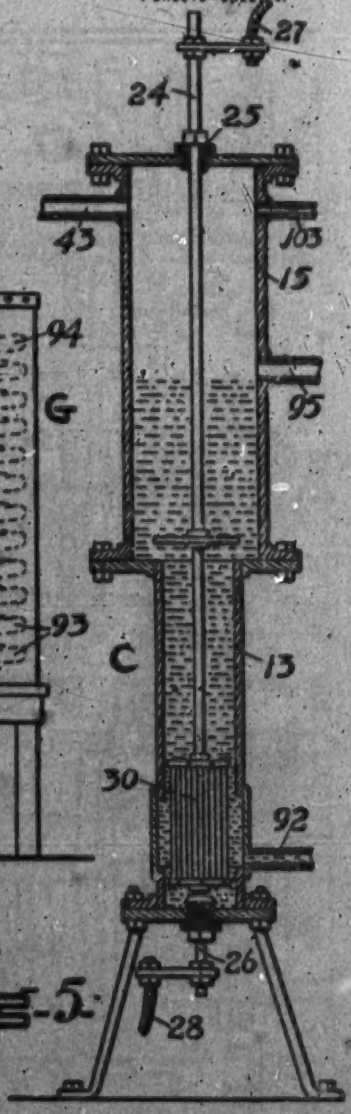

Fig. 5.

WITNESSES:

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PK 194-4

[fol. 1301] Patented Oct. 24, 1922. 1,433,519

United States Patent Office

Joseph H. Adams, of Flatbush, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Process for the Conversion and Transformation of Liquids, Fluids, and Oils

Original application filed December 1, 1909. Serial No. 532,842. Divided and this application filed December 5, 1917. Serial No. 205,527

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Flatbush, in the county of Kings and State of New York, have invented a new and useful Process for the Conversion and Transformation of Liquids, Fluids, and Oils, and of which the following is a specification.

This invention relates to processes of converting high boiling hydrocarbon oils to lower boiling products and is set forth and described, but not claimed, in my apparatus application S. No. 530,852 filed December 1, 1909 (U. S. Patent No. 1,320,354 granted October 28, 1919), of which this application is a division.

Furthermore, my present invention is a species which is covered broadly by my generic application S. No. 618,011 filed March 30, 1911, (renewal S. No. 289,425) Patent No. 1,327,263.

One of the objects of my invention, broadly considered, is to provide a process which may be practiced on a large commercial scale for converting high boiling hydrocarbon oils into lower boiling products, and which shall be particularly adapted for cracking large volumes of oil preferably supplied during the conversion process to a battery of highly heated converters which are operated concurrently to severally produce products of substantially uniform characteristics, this uniformity being insured by equalizing the pressures therein through the maintenance of the vapor spaces thereof in free and open communication and other-

wise operating the several converters under similar conditions.

Another more specific object of my invention is to provide a process in which a sufficient time is allowed to obtain the most effective conversion of the oils while applying moderate cracking temperatures, that consists in passing the oils successively through a series of concurrently operating cracking chambers, in each of which a portion of the oil is converted and from which the evolved converted vapors are withdrawn, condensed and collected.

Another object of my invention is to devise a continuous and expeditious oil conversion process, which shall be especially adapted for large capacity production, and in accordance with which extremely large volumes of oil may be treated continuously by passing the oil successively through a series of connected converters which operate concurrently to crack or convert the oil under superatmospheric pressure into the desired product which is constantly withdrawn from the several converters and then condensed and collected.

A still further object is to provide a process of the general character above indicated, which may be practiced on a large commercial scale with comparative safety to the apparatus as well as to the operators.

In accordance with the broad aspect of invention, the proposed process is carried out in connection with a plurality of converters that are subjected to cracking temperatures and which are operated concurrently t- convert large volumes of oil which are supplied thereto during their operation. The vapors evolved from the several converters are withdrawn as they are produced and are then condensed and collected. A uniformity in the vapors evolved by the several converters and in the ultimate products is secured by making provision for maintaining the converters under the same super-atmospheric pressure conditions through the establishment and maintenance of free and open communication between the vapor spaces thereof, whereby the operating pressures in the several converters are immediately equalized under all conditions of operation.

In a more specific aspect my invention contemplates a continuous process of cracking or converting oil in a plu-

rality of series-connected converters through which the oil traverses in succession, part of the oil being cracked in each of the converters and those portions which are not converted in one converter being passed on to the next adjacent converter of the series where further conversion takes place. In this way the oil is subjected to cracking conditions for a sufficient period of time to enable an exceedingly large proportion of the oil to be converted into the desired product. Moreover, by so dividing the actual conversion among a plurality of converters, it is entirely feasible to treat a very large volume of oil, while maintaining the con- [fol. 1302] verters of a size consistent with safety of operation, it being understood that the internal stresses upon the walls of a converter, imposed by the high pressures therein developed tremendously as the diameter of the converter is increased beyond certain safe limits.

These and other objects of the invention and features by which they are attained will become apparent to those skilled in the art from the following illustrative description of my process as carried out by certain specific apparatus or systems which are especially adapted for practicing the invention.

In order that my invention may be thoroughly understood I will now proceed to describe the same in the following specification and will then point out the novel features thereof in appended claims.

Referring to the drawings,

Figure 1 is an assembly view of a system embodying a converter adapted for use in carrying out my invention and other apparatus.

Figure 2 is an assembly in elevation, of an apparatus including only a single converter, but showing the supply and the collecting devices as arranged for carrying out my process.

Figure 3 illustrates a battery of converters showing the free communication of units, one to another.

Figure 4 is an end elevation of the battery converters showing one of the oil coolers and the vapor condenser.

Figure 5 is a sectional elevation of the converter shown in Figure 3.

In Figure 1, the containing vessel 1, of the supply apparatus A, may be somewhat elevated with respect to the

adjacent converter C, so that the gravitating tendency of the oil may augment its flow into the converter under the influence of the compressed air maintained over the surface of oil contained within the tank 1, to cause its delivery into the system against a back or vapor pressure maintained over the surface of oil and in the vapors while undergoing conversion and condensation in the converter and condenser.

A suitable frame 2, of wood or metal may be utilized as a support for this tank.

The fluid oil may be admitted into the containing vessel or tank 1, by means of one or more suitable supply pipes indicated by 3, and controlled by valve 4, and when admitting oil the displaced air may escape through pipe 5, controlled by valve 6. This tank is provided with glass sight gauges 8, so that the oil level therein may be constantly under observation.

A pipe 9, connects the supply tank and converter C, in any desired manner and in order to control the delivery of oil into the converter the valve 10, is provided in the pipe line 9, for this purpose.

As a means of drawing off oil from the tank, the pipe 11, controlled by valve 12, is provided below the pipe fittings under the tank, and in order to supply compressed air to tank 1, pipe 8, leading out from a T fitting in pipe 3, and controlled by valve 8', leads to a compressor or suitable supply of compressed air so that a compression may be employed over the surface of oil in tank 1, to cause its delivery into the converter against a back or vapor pressure maintained therein.

The converters C proposed for use in this invention may assume diverse forms without undergoing an essential difference in character.

The converter shown in Figure 1, which may constitute one of a battery of converters, comprises a retort or heating section 13, provided with a glass sight gauge 14, and surmounted by a cylindrical crown or dome 15, also provided with a glass sight gauge 16.

Preferably, but not necessarily, the supply pipe 9, in this form leading from the supply tank 1, will lead into the upper part of the retort or section 13, which section forms the lower part of the converter C.

This lower section is provided with a pipe 17, controlled by a valve 18, so that when occasion so demands, the retort may be emptied and cleaned of any heavy oil or sediment which may have accumulated therein, and the heavy residual oil may be withdrawn from time to time during the operation of the system.

The crown cylinder 15, is secured to the retort 13, by means of a suitable interposed flange member 20, which is bolted to each of them.

Inasmuch as the vapors rising into and filling the crown or dome 15, exert a high pressure, I have arranged a cap 21, in close fitting relation with the upper end of the cylinder crown or dome, and have utilized as a means for securely retaining the cap in position a number of strong steel bolts which will hold this cap securely to the top of the dome. The lower section or retort may be connected with the overlying dome by means of a gauge column 22, on which glass sight gauges 23, are arranged so that the condition and disposition of the contents of the converter C, may always be the more readily apparent and be susceptible of an intelligent variation.

A feature of importance is the means for internally applying heat to the oil contained in the retort while held under a self-imposed super-atmospheric vapor pressure for the purpose of bringing about a conversion of such oil.

Preferably, this feature is electrically operated, and [fol. 1303] comprises one or more resistance rods, which are adapted to be maintained at a heat sufficient to crack and convert the oils undergoing treatment while submerged within the oil.

By controlling the electric current, the electric heater may be maintained at any predetermined temperature as rendered desirable by the conditions of operation.

This electric heater is especially adapted for working under an electric current having relatively low voltage and correspondingly high amperage. The current is brought in by means of a metallic conductor rod 24, which passes through the cap 21, at the summit of the dome 15, and in order to prevent grounding or short circuit of the current, an insulating bushing and gland 25, of suitable material such as soapstone or long fibre asbestos composition will be interposed in a tight fitting relation between such cap and the leading in conductor rod 24.

So also, a leading out conductor rod 26 may similarly pass through the bottom of the retort section 13, and the current for operation will be taken from the mains 27 and 28, as will be observed.

It will be understood that during the operation the raw or unconverted oils will be relieved of more or less of the carbon of which they are in part composed. This, of course, alters their chemical character and converts them from one or more of the products of the hydrocarbon series into others of an essentially different character. The carbon which is removed in this manner will be in part deposited on the highly heated electrodes and in part precipitated in the adjacent oil, being to some extent held in suspension and to some extent gravitated through the oil toward the bottom of the converter. The heavy residual oil containing this gravitated carbon may, of course, be withdrawn as desired through the pipe 17 and valve 18.

Mixed vapors of the orignal and the cracked oil are evolved very rapidly owing to the intense heat of the resistors and consequently care should be exercised to keep the oil line at the proper mark in the gauge and not to permit it to fall below or approach the top of the electric heater for the resistors would protrude above the level of the oil and an uneven heat would be the result, the upper or exposed part becoming hottest where there was the greatest resistance to the radiation of heat.

The mixed vapors pass from the dome or crown cylinder 15, into the vapor discharge pipe 43, and thence through the pipe 44, into a suitable condenser E, of which 45, are the cooling coils, contained within a tank 45', and mounted on a suitable support 46, if desired.

Since some of the vaporized original oil may tend to condense before reaching the condensing apparatus E, I prefer to connect the vapor discharge pipe 43, with the bottom of the retort 13, by means of the gauge column 22, and in this manner utilize this tube member for two purposes. This will enable the preliminary condensed unconverted oil to be readily passed through the retort again. I also prefer to provide a safety pop valve 47, mounted above the condenser E, and in an elbow of the pipe 44, so as to relieve any sudden or excessive pressure above the pre-determined vapor pressure under which the process is operating.

I may also place in the vapor line 43—44, a thermometer or pyometer 48, so that the temperature of the converted vapors passing over to the condenser may be under observation.

After passing through the coil condensing apparatus E, the fluid oil passes into and is collected within a reservoir F, of which the container 49, is the tank, by means of pipe 50, shown in Figs. 1, 2 and 3.

The upper part of this reservoir F, is provided with a gas vent pipe 51, controlled by a needle valve 52, and the lower part is provided with a liquid draw off pipe 53, controlled by valve 54.

A glass sight gauge 55, is located on this tank 49, so that the surface level of oil may be noted, and a pressure gauge 56, provided at the upper part of the tank so that vapor pressures within the system can be under constant observation to make it possible for the operator to be informed when to the the built up pressure by opening the needle valve 52, in pipe 51.

A draw off tap 57, is located in pipe 50, at the foot of the condenser E, for the purpose of taking samples of distillate from time to time during the operation of the process.

The utility of the gas vent pipe 51, and valve 52, in conjunction with the other features of my invention are very great for, thereby, I am enabled to regulate the pre-determined vapor pressure in the apparatus and promote uniformity and certainty in the operation of the entire apparatus from the source of supply through to the end of or beyond the condenser.

As a means of regulating the temperature of the condensing coils 45, of the condenser E, I have provided a cold water inlet pipe 58, and an overflow pipe 59, for the discharge of the heated water which accumulates at the top of the tank; and as a means of observing pressure in the supply tank 1, I have provided a pressure gauge 60, at the top of the tank. I have also provided a pressure gauge 61, at the top of crown or dome 15, so that the pressures in the converter may be known as well as the discharge end in [fol. 1304] tank F, when the apparatus is working under satisfactory conditions both gauges 56 and 61, should register the same uniform pressure throughout the system

from the valve 10, in pipe 9, through the condenser and into the collecting apparatus F.

The above specifically described apparatus was employed by me in connection with the conversion of light oils, as kerosene, into naphthas and gasolenes at high or cracking temperatures while the oil undergoing treatment and the vapors being condensed were held under super atmospheric vapor pressures.

Another and more commercially practical apparatus is shown in Fig. 2, which, as a unit or in a battery as shown in Fig. 3, comprises an efficient system for transforming high boiling oils into lower boiling products. The system of Figures 2 and 3 consists of the various co-related parts shown and described in Fig. 1, but in place of the use of compressed air maintained over the surface of oil in the supply tank 1, a pump 62, is provided to withdraw oil from the supply tank and force it into the converter C, through a pre-heater B, against a back or vapor pressure maintained in the pre-heater B, converter C, condenser E and running tank F.

Inasmuch as it is desired to conserve heat energy as much as possible in this apparatus, the comparatively cold oil flowing through the pipe 9, is preferably caused to pass through the oil pre-heater B, and thus be raised in temperature before passing into the oil converting receptacle. This pre-heater may be of any suitable type but preferably provides a continuously rising coil 63, connected with the outlet pipe 64, which is located at the top so that any air bubbles may readily escape and not form air locks in such pre-heating coil. The source of heat for said pre-heater may be the oil returning from the converter and hot oil receivers at the opposite side of the apparatus or it may consist of any other heat supplying means.

The converter in this type of apparatus comprises the retort 13 and overlying dome 15, and an underlying chamber 65, provided with a detachable plate 19, for receiving the heavy bottoms, carbon and other residues. The accumulated residuum may be drawn off through pipe 17 and valve 18.

The means for admitting oil to the converting receptacle is shown as pipes 66 controlled by valves 67, and 68 controlled by valve 69, and by this means oil may be delivered into the upper or lower part of the converter, as a matter of choice.

This converting receptacle may be supported by suitable legs or supports 70, and like the converter of Fig. 1, will preferably consist of a number of sections bolted together in fluid-tight connections.

The heavy bottoms chamber 65, is formed of a pipe-like section having the bottom plate 19, provided with an insulating bushing 71, tightly fitting in a central aperture. This bushing, like 25, at the upper end of the retort, tightly encircles the vertical conductor rod 26, and insulates the same from the metal of the receptacle.

A suitable thermometer or pyrometer 72, may be arranged in permanent relation with the retort 13, and another one 73, with dome 15, so that the temperature of the oil contained therein may be kept under constant observation.

As has been stated, the branch line feed pipes 66 and 68, may enter the converter as shown, and also a branch line pipe 74, having a valve 75, may connect such converter with a return pipe 76, to enable a flow to take place as will be subsequently described.

The vapor dome 15, comprises a drum like section having one inlet 66, for the oil coming from the supply tank 1, through the coils 63 of the heater B, and pipe 64, and an outlet pipe 77, controlled by valve 78, for overflow unconverted hot oil.

It may here be stated that since the process of conversion depends upon subjecting oil or oily vapors to very high temperatures considerably above their vaporizing points, and since this evidently cannot be done without volatilizing in unconverted form large quantities of such oil it will be necessary to maintain high self-generated vapor pressures within the system and to re-treat such fractions as have escaped the action of the process.

By arranging the electric heater in the manner described, it is possible to materially reduce the escape of unconverted oils, but nevertheless, it has been found that considerable quantities pass through the converting receptacle without having been materially affected. Such oils being comparatively heavy, may be readily condensed or caught by properly arranged baffle plates, and to this end this invention proposes a structure or system of parts intervening between the converter and condenser for the converted frac-

tions and the un-converted oils which are to be collected and returned for re-treatment.

In this embodiment a vapor trap 79, having a baffle plate 80, intercepts the vapors escaping from the upper part of dome 15, and any heavy parts not light enough to go down and around the baffle plate 80, and out through pipe 44, are led back into the converter through pipe 76.

The oily vapors and particles of heavy oil from the converter pass out through the pipe 43, and are projected against the plate 80, and this action, as in a steam trap, collects the heavy particles, condenses and throws them [fol. 1305] down in liquid form. Such vapors as have escaped condensation in the trap 79, pass through pipe 44, to a suitable condenser E, capable of condensing all products which may have a liquid form at ordinary temperatures.

A pop release valve 47, is provided in this form of apparatus and it is located over the condenser E, in the pipe 44, to insure safety in case the pressure should exceed a pre-determined number of pounds to the sq-are inch under which the apparatus is working normally.

This apparatus may be operated with the oil flowing either upwardly or downwardly past the electric heater as a matter of choice. Thus, when operating with a down-flow of oil, valve 69 in pipe 68, is closed as well as valve 78 in pipe 77. The incoming oil will then flow through pipe 66 and valve 67, into the dome 15, and passing down through the retort 13, it is led out through pipe 74 and valve 75, then rises in pipe 76 and overflows into tank 82 through pipe 81.

This hot oil overflow tank 82, is provided with a glass sight gauge 83, so that the height of oil therein may be known in order to indicate when the valve 85 in pipe 84, should be opened to draw off the hot oil into the collecting apparatus D, of which 86, is the tank provided with glass sight gauges 87. Oil may be withdrawn from this collecting apparatus D, by means of pipe 88, when pump 89, which latter will force the oil through pipe 90, and past check valve 91, into supply tank 1, for re-treatment with new oil.

The converted vapors will pass through the trap tank 79, and other parts as described, the distillates and gases

being caught in the running tank F, located beyond the condenser.

In case it is desired to have the flow upwardly past the heater, valve 67 in pipe 66, and valve 75 in pipe 74, will be closed while the valve 69 in pipes 68 and 78 in 77, will be opened. In this manner oil flowing through pipe 68, and up through retort 13, will overflow through pipe 77, into tank 82, from which it is drawn into collecting apparatus D, and returned to supply tank 1, by means of pump 89, as described. The vapors passing off through pipe 43, trap 79 and condensing coils 45, are reduced to distillates and collected as described.

Figures 3, 4 and 5, illustrate another form of apparatus for practicing this invention on various grades of oil by causing large volumes of oil to be supplied during the cracking process to a battery of converters that are severally operated at cracking temperatures and super-atmospheric pressures to concurrently effect the conversion of oil in said converters into like vapors that are withdrawn, condensed and collected, the pressures in the several converters being equalized by maintaining the vapor spaces thereof in free and open communication. In the particular apparatus shown for illustrative purposes the oil is first passed through a preliminary converter, then through a suitable cooling coil if desired, and thereafter through one or more re-treating converters and cooling coils. In this manner the oil may successively course through a series of two or more converters freely connected one with another, whereby oil is concurrently cracked and converted in each of the converters.

Although a particular form of converter is illustrated in Figs. 3, 4 and 5, it is to be understood that any of the types of converters shown in the drawings, and, in fact, any converter constructed and arranged for performing the cracking function may be employed. As shown, the several converters are independently and internally heated by means of suitable electric heaters, which may be so regulated by controlling the current flowing therethrough as to produce the requisite heat for the conversion process under the existing conditions. Obviously, the invention, broadly considered, is not restricted to the use of internal electric heat and any means of maintaining the converters at the desired cracking temperatures may be utilized.

In Fig. 3, a battery of converters is shown where the vapor outlets connect into a common vapor line 44, leading to the condenser E. In operation, the oil to be treated enters through the pipe 66, and flows into the dome 15, thence downwardly into the retort 13, of the first or right hand converter C^1, and past and into intimate contact with the hot electrodes of the electric heater and thence out through pipe 92, (see Fig. 4,) into the lower end of the coils 93, of the cooling apparatus G.

By entering at the lower end of this coil, the oil and gases are able to rise therethrough without interruption and without the likelihood of forming air pockets. The upper end 94, of the coil 93, is connected with a pipe 95, leading into the next converter C^2, of the battery. The oil then passes down through the converter past the intensely heated electrodes thereof and into a second cooling coil in the apparatus G, then into a third retort C^3, and so on through other coolers and converters, if desired.

The use of the coolers interposed between the several converters is not at all essential to the operation of the invention, and is not intended to make the oil cold by any means, but merely to insure that the temperatures are not superposed to such a degree that the oil will be overheated and changed into fixed gas instead of cracked into light products as desired.

Ultimately, the oil passing through the series emerges [fol. 1306] from the last cooling coil through the pipe 96, preferably, provided with a valve 97, and from this pipe it may be run into an enclosed collecting tank as 86, of apparatus D, (Fig. 2,) and returned to the system for re-treatment, if desired.

Returning now to the first converter, C^1, the course of the vaporized products may be followed:

The major proportion of the vapors evolved in the first converter C^1, will rise through the vapor dome 15, and pass out through the pipe 43 at the upper end of such dome. The vapors must rise a short distance through the stand pipe 98, and the precipitated unconverted residue may flow back through the pipe 99, and be returned to the action of the electric heater. The vapors then rise through the stand pipe 98, and past the release pop valve 100, which will be operative in case the pressure suddenly and unduly increases, and then will flow downwardly through the elbow

pipe 101, into the inclined vapor pipe or main 44. The successive converters are connected in like manner and severally discharge their converted products into the common main which leads to the condensing apparatus E, and from which the converted products run into the collecting trap tank 55, through pipe 50.

Fig. 5, represents in vertical section the construction of one of the converters as shown in Figs. 3 and 4, and illustrates the very simple combination of parts comprising a converter. This form is provided with the electric heater at the lower part of the retort 13, and positioned opposite a sight glass 102, in the lowermost narrow portion of the converting receptacle.

From the foregoing description of the illustrated apparatus it will be understood that the several converters constituting the battery are connected in series relation by means of suitable flow line pipes through which the oil traverses, and, moreover, the vapor spaces of the converters are also connected by vapor line pipes to a common vapor main which delivers the evolved vapors to the condensing apparatus and collector. This inter-connection of the vapor spaces of the converters is of particular importance in serving, to equalize the pressures on the several converters and thus insure substantially constant oil levels therein and uniformity of the evolved vapors.

Since all of the converters are maintained at a cracking temperature, and under superatmospheric pressure, a portion of the oil which passes through them in succession is cracked or converted in each of the units of the battery, while that portion which is not converted in any one of the converters is eventually passed on to the next adjacent converter, where it is further subjected to cracking temperatures and in which further portions of the oil are converted. In this manner, the oil courses successively through the several units of the battery and it is thus subjected to cracking temperatures for a considerable period of time, thereby resulting in the conversion of relatively large amounts of the oil. While the oil is thus acted upon successively by the several converters as it passes through them, it will be understood that all of the converters operate continuously upon that portion of the oil contained therein, so that the evolution of converted vapors in the converters takes place concurrently and is subsequently withdrawn, condensed and collected.

With this multiple or battery arrangement of converters relatively large volumes of oil may be treated continuously, while the size of the individual units may be held within safe limits.

One or more of these receptacles may be provided with a pipe 103, leading to a pressure gauge 61, so as to enable the operators to be constantly informed as to the pressure under which the apparatus is working.

Thus, it will be seen that when operating under super-atmospheric pressures, the high heat of the electric heater raises the temperature of the oil and oily vapors above that required only to volatilize the oil and self-generated vapor pressures in excess of atmospheric pressure will be the result.

It will be noted that in each of the collective drawings Figs. 1, 2, 3 and 4, the converters are in free communication with the condensers and running trap tanks for the accumulation of distillates and fixed gases, and that the super-atmospheric vapor pressures generated in the converters extend to and through the condensers and running trap tanks located at the foot of or beyond the condensers.

While I have, for illustrative purposes, set forth the process of my present invention in connection with apparatus of a more or less specific character and as embodying certain definite steps and mode of procedure, it will be understood that my invention is not so restricted, and that omissions and variations in the steps of the process may be made without departing from the spirit and scope of the invention. Therefore only such limitations should be imposed as are indicated in the appended claims.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbons which comprises continuously passing the oil to be treated under pressure successively through a plurality of heating chambers connected in series, maintaining vapor pressure in each of [fol. 1307] said chambers on said oil, and drawing off the vapors from each of said chambers.

2. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbons which comprises continuously passing the oil to be treated under pressure

successively through a series of heating chambers connected in series, maintaining a vapor space in each of said chambers above said oil, maintaining free and open communication between the vapor space of said chambers, passing the vapors through a condenser and maintaining vapor pressure in said chambers to and through the condenser.

3. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbon which comprises supplying oil under pressure to a series of separate converting chambers, heating said oil in said chambers to cracking temperatures, maintaining vapor spaces in said converters above the oil, maintaining free and open communication between the vapor spaces of said chambers, maintaining self-imposed vapor pressure in said chambers, and condensing the vapors.

4. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbons which comprises supplying oil under pressure to a series of separate converting chambers, heating said oil in said chambers to cracking temperatures, maintaining self-imposed vapor pressure in said chambers, and passing the vapors evolved in the several converters to and through a condenser under substantially the same pressure as that in the chambers.

5. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbons which comprises continuously passing the oil to be treated under pressure successively through a plurality of heating chambers connected in series, maintaining a vapor space in each of said chambers above said oil, maintaining free and open communication between the vapor spaces of said chambers, and condensing the vapors under the self-imposed vapor pressure generated and maintained in said chambers and extending through the condensing means.

6. A process of treating high boiling hydrocarbon oils to obtain lower boiling point hydrocarbons which comprises supplying oil to a plurality of heating chambers, heating the oil in said chambers to cracking temperatures, maintaining a vapor space in said chambers above said oil, maintaining open communication between the vapor spaces

of said chambers, condensing the vapors and maintaining substantially the same vapor pressure in said chambers to and through the condensing means.

7. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises supplying oil to a plurality of converters, subjecting the oil in the several converters to sufficient cracking temperatures and super-atmospheric pressures to effect concurrent conversion of oil contained therein, equalizing the pressures in the several converters by maintaining free and open communication between the vapor spaces thereof, and withdrawing the evolved vapors from the several converters.

8. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises supplying oil during the cracking operation to a plurality of converters, heating the converters to cracking temperatures while maintaining self-imposed super-atmospheric vapor pressures therein whereby oil in the several converters is concurrently cracked, equalizing the vapor pressures in the several converters by maintaining free and open communication between the vapor spaces thereof, and withdrawing the vapors as they are evolved in said converters.

9. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously supplying oil to a plurality of concurrently operating converters, subjecting the oil in the several converters to cracking temperatures and super-atmospheric pressures generated by evolved vapors, and continuously withdrawing from the several converters the vapors as they are evolved therein, while establishing uniform pressures in the several converters by maintaining the vapor spaces thereof in free and open communication whereby any unbalance of vapor pressure is immediately equalized.

10. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises supplying oil to a plurality of converters, subjecting the oil in the several converters to cracking temperatures under equalized super-atmospheric pressures whereby oil in said converters is concurrently converted under substantially uniform operating conditions into substantially like vapors, condensing the converted vapors and collecting all of the condensed converted vapors to form the desired product.

11. A process of converting high, boiling hydrocarbon oil into lower boiling products that comprises supplying oil to a plurality of converters, subjecting the oil in the several converters to sufficient cracking temperatures and super-atmospheric pressures to effect concurrent conversions of oil contained therein, equalizing the pressures in the several converters by maintaining free and open communication between the vapor spaces thereof, withdrawing the evolved vapors, separating out the heavy unconverted portions and returning cycic-ly them for re-treatment, and condensing and collecting the converted vapors.

[fol. 1308] 12. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises supplying oil during the conversion process to a plurality of converters subjected to cracking temperatures and super-atmospheric pressures, equalizing the pressures and the oil levels in the several converters by maintaining free communication between the vapor spaces thereof, and withdrawing the evolved vapors from the several converters.

13. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing the high boiling oil in succession through a series of connected converters, cracking or converting the oil in the several converters concurrently by subjecting the oil therein to cracking temperatures and super-atmospheric pressures, and separating the vapors evolved in each converter from the oil therein and withdrawing the same.

14. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession through a series of connected converters that are severally maintained at substantially uniform super-atmospheric self-imposed vapor pressures and cracking temperatures, whereby oil in each of the converters is cracked, and separating the vapors evolved in each converter from the oil therein and withdrawing the same.

15. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession through a series of connected converters, maintaining the several converters at cracking temperatures whereby the oil in the several converters is

concurrently cracked, equalizing the pressures on the several converters by maintaining free and open communication between the vapor spaces thereof, and withdrawing, condensing and collecting the vapors evolved in each of the converters.

16. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing the high boiling oil in succession through a series of connected converters, maintaining the converters at sufficient temperatures and under sufficient self-imposed vapor pressures to concurrently crack the oil therein as it progressively traverses through them, and separating the vapors evolved in each converter from the oil therein and withdrawing the same.

17. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession through a series of con-ected converters, heating the converters under self-imposed vapor pressure to severally maintain them at a cracking temperature whereby conversion takes place concurrently in the several converters, withdrawing the evolved vapors, separating out the heavy unconverted portions and cyclicly returning them for retreatment, and condensing and collecting the converted vapors.

18. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession under super atmospheric pressure through a series of connected and highly heated converters whereby oil is concurrently cracked in each of the converters, concurrently withdrawing the evolved vapors from the several converters, and returning to the series of converters for retreatment the unconverted oil delivered therefrom.

19. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing a stream of fresh high boiling oil through a series of connected converters maintained at cracking temperatures and super-atmospheric pressures whereby a portion of the oil is cracked in each of the converters, withdrawing and condensing the evolved vapors from each of the converters, and creating a cyclic operation by returning the unconverted

oil to the first converter of the series while maintaining the supply of fresh oil whereby the returned oil is mixed with the fresh oil and retreated.

20. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing the high boiling oil in succession through a series of connected converters maintained at cracking temperatures and super-atmospheric pressures, withdrawing and collecting the vapors evolved from the several converters, and partially cooling the oil as it passes from one converter to another.

21. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession through a series of connected converters, subjecting the oil in the several converters to substantially uniform superatmospheric pressures and cracking temperatures, while maintaining a substantially uniform oil level in said converters as the oil progressively traverses through them and is cracked, whereby the several converters operate concurrently and under substantially like conditions to severally produce substantially like vapors and withdrawing the evolved vapors from the several converters.

22. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil in succession through a series of connected converters, subjecting the oil therein to cracking tempera- [fol. 1309] tures and super-atmospheric pressures and equalizing the pressures and the oil levels in the several converters by maintaining free communication between the vapor spaces thereof.

23. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises preheating the oil, passing the oil in succession through a series of connected converters, maintaining cracking temperatures and super-atmospheric pressure in the converters whereby the passing oil is converted, withdrawing the evolved vapors from the several converters, and separating out the heavy unconverted oil and returning it for reheating and retreatment.

24. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil through a series of connected converters successively, subjecting the oil to heat by heaters disposed within the converters under self-imposed vapor pressure to effect concurrent cracking of the oil therein, and immediately withdrawing the vapors evolved in the several converters.

25. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises passing the high boiling oil through a series of connected converters severally heated to substantially like temperatures sufficient to effect a conversion of the oil therein whereby the converters operated concurrently under substantially like temperature conditions to produce substantially like vapors, and withdrawing the evolved vapors from the several converters.

26. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing the high boiling oil in succession through a series of connected converters, independently electrically heating the several converters to temperatures sufficient to effect a conversion of oil therein, and withdrawing the evolved vapors from the several converters.

27. The process of converting high boiling oils into lower boiling products which comprises continuously passing the oils through a plurality of converters provided with vapor spaces and having direct communication the one with the other for determining the oil levels therein, and permitting the oil to flow through them successively, heating the several converters under self-imposed superatmospheric pressures to cracking temperatures, maintaining equalized pressures in the vapor spaces of the converters by establishing free and open communication between them at points above the liquid flow and oil level communication, and removing and condensing the evolved vapors from said converters.

28. The process of converting high boiling oils into lower boiling products which comprises continuously supplying oil in liquid form to the first of a plurality of series-connected converters maintained at cracking temperatures and

under super-atmospheric self-imposed pressures and operating concurrently upon the oil in transit there-through, separating the unconverted oil from the evolved vapors in each preceding converter of the series and supplying it to the next succeeding converter thereof for further treatment, withdrawing the converted vapors of desired volatility as fast as formed from the several converters, and condensing said converted vapors under the same pressure as maintained within the converters during the cracking operation.

In testimony whereof I affix my signature in the presence of two witnesses.

Joseph H. Adams.

Witnesses: A. Capstich, Joel S. De Selding.

4734

[fol. 1310]

PETITIONER'S EXHIBIT 195

Mar. 13, 1923. 1,448,254

W. M. BURTON ET AL.

PROCESS OF TREATING PETROLEUM OILS

Filed Mar. 2, 1916 2 sheets-sheet 1

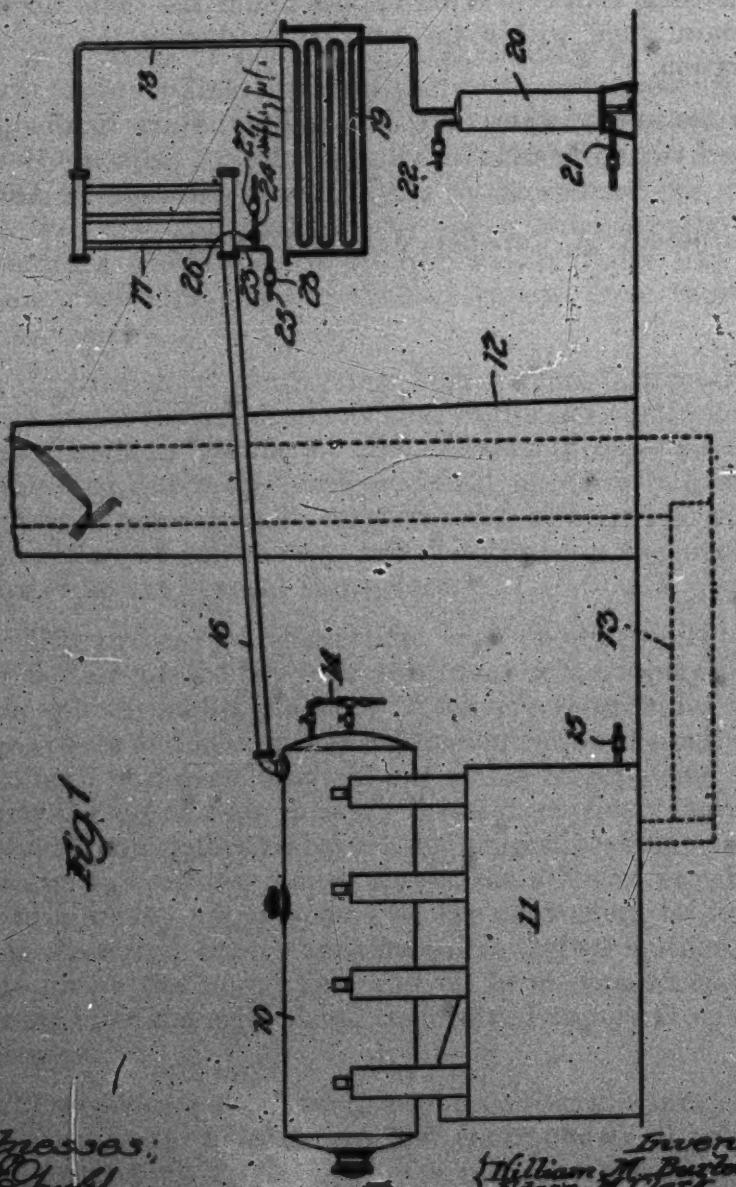


Fig 1

Witnesses:

Inventors:
William M. Burton
Edgar M. Clark.

PX 195-2

4735

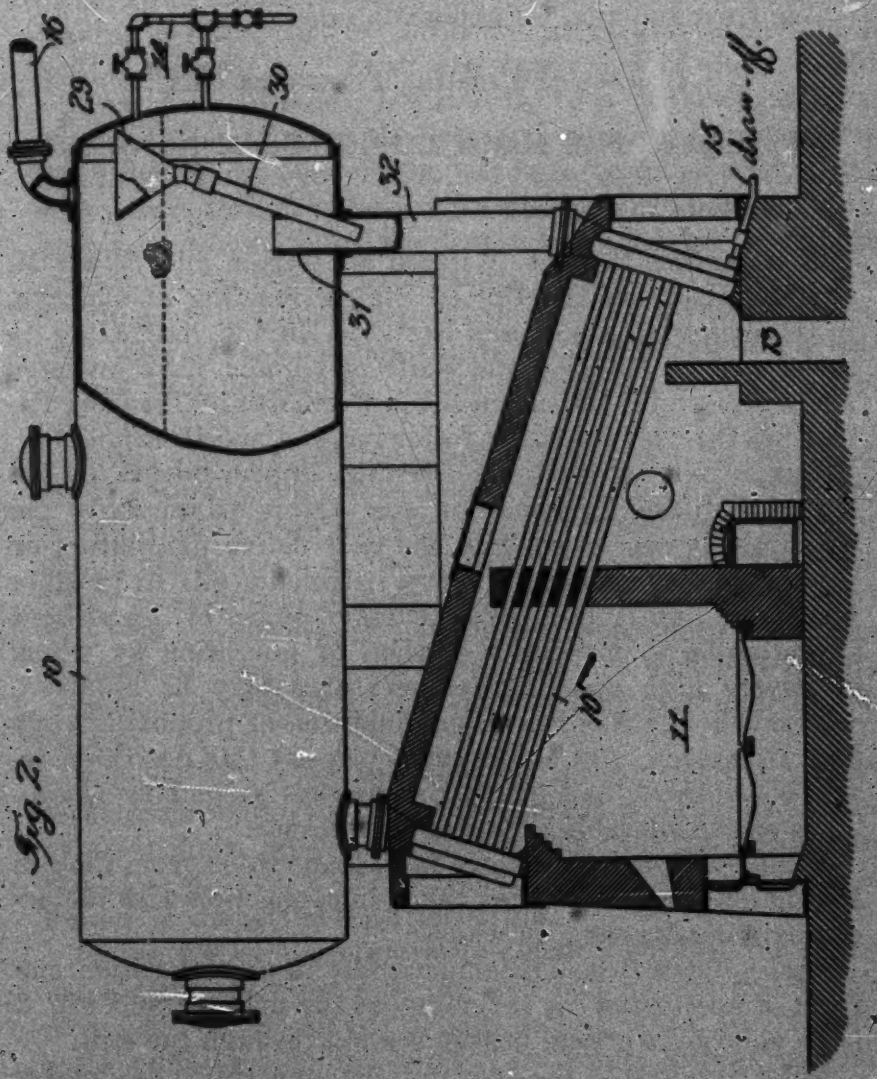
[fol. 1311]

Mar. 13, 1923. 1,448,254

W. M. BURTON ET AL

PROCESS OF TREATING PETROLEUM OILS

Filed Mar. 2, 1916 2 sheets-sheet 2



Witnesses:

Inventors:
William M. Burton
Edgar M. Clark.
By Dyer, Brown & Clarke, Their Attys.

[fol. 1312] Patented Mar. 13, 1923. 1,448,254

United States Patent Office

William M. Burton, of Chicago, and Edgar M. Clark, of Alton, Illinois, Assignors to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Process of Treating Petroleum Oils

Application filed March 2, 1916. Serial No. 81,665

To all whom it may concern:

Be it known that we, William M. Burton and Edgar M. Clark, citizens of the United States, residing at Chicago, in the county of Cook, and State of Illinois, and Alton, in the county of Madison and State of Illinois, have invented a new and useful Improvement in Processes of Treating Petroleum Oils, of which the following is a specification.

Our invention relates to certain improvements in the art of distilling hydrocarbon oils. More particularly the invention is concerned with the destructive distillation or "cracking" of relatively heavy petroleum oils to produce therefrom lighter oils. The primary object of the present invention is to provide a method of operation by which relatively high cracking temperatures may be obtained, without the usual concomitant condition of proportionately high pressures. By our present process this desirable result is obtained, and likewise numerous secondary advantages of considerable practical importance.

The invention will be more fully understood from the following detailed description taken in connection with the accompanying drawing, in which:

Fig. 1 illustrates diagrammatically in side elevation one form of apparatus for carrying out the process, and Fig. 2 is an enlarged vertical broken section through the still.

Referring first to the drawing, the numeral 10 designates the drum of a suitable still, which as illustrated is of the horizontal tubular type, the tubes designated 10′, being located within the furnace 11. A stack 12 is connected with the furnace as by an underground flue 13. The external fittings of the still include the usual gage 14 and draw-off

15, the latter being connected through the furnace wall with the lowest point of the rear tube header so that the drum and tubes may be completely drained, as is well understood.

Leading from the still at an upward inclination is a combined vapor outlet pipe and reflux condenser or dephlegmator 16 of proper dimensions, and for increasing the condensing capacity of the latter we preferably surmount it with a radiator 17. From the upper end of the radiator a vapor pipe 18 leads downwardly to a water-cooled condenser 19, and below the latter is arranged a receiving drum 20 for the condensate. It is to be noted that in the arrangement shown the entire system including the still, dephlegmator, radiator, condenser and receiving drum is in open communication throughout. The receiving drum is provided with a valved liquid drain 21 and a valved gas escape pipe 22, and by this construction the contents of the system may be brought to and maintained at any desired pressure.

At the end of the dephlegmator 16 adjacent to the radiator 17 a supply pipe 23 is tapped thereinto which pipe may be split into two branches 24, 25, the former being provided with a check valve 26 and control valve 27, and the latter, which is employed as a drain only, having a cut-off valve 28. The supply branch 24 will lead to a pump or storage chamber or reservoir having a pressure sufficient for the introduction of the fluid into the dephlegmator, as will later appear.

Immediately below the elbow of the dephlegmator there is mounted within the drum 10 a funnel 29 (Fig. 2) carried by an inclined pipe 30 which projects into the upstanding end 31 of the rear vertical trunk 32 by which the rear tube header is connected with the drum.

In the use of the apparatus above described for carrying out our new process, the still will be charged with a petroleum oil of relatively high boiling point, for instance a stock having a boiling point of its lowest substantial fraction approximating 600° F. at atmospheric pressure. The still will then be fired and the contents heated up to a point at which distillation proceeds slowly under a pressure of upwards of four and preferably about seven atmospheres, this pressure being maintained not only upon the liquid

in the still but preferably also throughout the system under the control of the valved gas escape pipe 22, as in the patent to William M. Burton, one of the present applicants, [fol. 1313] No. 1,049,667, of January 7th, 1913. The temperature of the liquid body and the vapors in the still will then be approximately 750° F., the temperature of the vapors being progressively less along the length of the dephlegmator.

When this condition has been reached we begin to feed in through the supply pipe 24, a stock of oil of mean boiling point substantially lower than that of the stock in the still, for instance "bottoms" from the redistillation of crude gasolene made by the process of the Burton patent before referred to. Such bottoms range in boiling point (at atmospheric pressure) from about 400° to 500° or thereabouts. Under the pressure of seven atmospheres maintained in the still and its connected condenser the boiling point of this stock would be about 600° to 700° F., which would be too low to effect any considerable cracking, especially since these "bottoms" have already been subjected to one cracking operation the result of which is to render them quite refractory.

As this cold stock, entering through the pipe 24, passes downwardly through the dephlegmator and becomes mixed with the reflux condensate therein, its temperature is gradually raised, the rise being sufficient to bring the stream almost to its boiling point at the time it leaves the lower end of the dephlegmator to drop into the funnel 29. The lighter portion of the mixed stream, including substantially all of the in-fed stock is thereupon instantly flashed into a vapor by coming into contact with the hot body of oil. This vapor instead of remaining at its boiling-point temperature of 600° to 700°, becomes instantly superheated by the liquid body of the still charge and the high-boiling-point vapors thereof, being thus brought to the temperature of the still in spite of the fact that its normal boiling point temperature under the pressure obtaining in the still is materially below the temperature of the latter. This superheating of the vapors of the low-boiling-point stock by the liquid body and vapors of distillation of the high-boiling-point stock, is the result aimed at by our process. Under these conditions the temperature required for cracking the

low-boiling-point material is obtained without the employment of proportionately high pressures, and without resort to superheating tubes, flash-plates, red-hot refractory earth masses, molten metal baths, or any of the recognized expedients for superheating vapors. Whatever proportion of the mixed stream entering the funnel 29 fails to be vaporized therein is conducted directly downward into the hot tubes 10, being thereby subjected immediately to the highest temperature available.

Our process may be carried out with the ordinary apparatus used for pressure distillation and therefore commends itself to practical refiners as involving no untried expedients but only safe and economical methods of proven value.

It is to be noted that in the operation set forth above the charge of relatively high-boiling-point stock within the still is itself subjected to a cracking operation simultaneously with its use as a "superheater" for acting upon the lighter stock fed in. It will be apparent that the exact extent of this cracking of the still charge will depend upon the nature of that charge, i. e., it may be composed of such refractory constituents as to dissociate only to a small degree under the temperature and pressure conditions obtaining in the still, or it may be of such a nature as to crack at the ordinary rate under these conditions.

It will be understood that the cracked vapors of the infed stock will pass outwardly through the dephlegmator, and thence to the condenser and receiving drum in the usual manner.

While we have described in considerable detail one specific manner of carrying out the novel steps of our process, it is to be understood that this description is illustrative only, and for the purpose of making our invention more clear, and that we do not intend that our invention shall be construed as limited to these details except in so far as we have included such limitations within the terms of the following claims in which it is our intention to claim all novelty inherent in our process as broadly as is permissible in view of the prior art.

What we claim as new and desire to secure by Letters Patent is:

1. The process of distilling petroleum hydrocarbons which consists in heating a liquid body of such hydrocarbons above its atmospheric boiling point under a pressure of upwards of four atmospheres to effect distillation thereof, and feeding into such liquid-body from an extraneous source a fresh stock of hydrocarbon having a boiling point under the prevailing pressure lower than the temperature of the liquid body, thereby superheating and cracking the infed material.

2. The process of cracking refractory petroleum hydrocarbons which have previously undergone one cracking operation which consists in heating a liquid body of hydrocarbons having a boiling point above that of the refractory stock to a temperature exceeding the boiling-point of the latter, and introducing the refractory stock from an extraneous source into such heated mass, thereby superheating and cracking the same.

3. The process of distilling hydrocarbons for the pyrogenesis of lower boiling point hydrocarbons which consists in maintaining a body of the hydrocarbons in a receptacle under super-atmospheric pressure, and flowing a stream of [fol. 1314] said hydrocarbons through a heated zone to said receptacle, thereby maintaining a vaporizing temperature in the receptacle, and supplying to said flowing stream from an extraneous source hydrocarbons having a boiling point under the prevailing pressure lower than that of the body of hydrocarbons.

4. The process of distilling hydrocarbons for the pyrogenesis of lower boiling point hydrocarbons which consists in maintaining a body of the hydrocarbons treated in a receptacle under the superatmospheric pressure, flowing a stream of said receptacle, thereby maintaining a vaporizing temperature therein, cooling the vapors evolved to condense their heavier constituents and supplying this condensate to said flowing stream together with additional hydrocarbons from an extraneous source having a boiling point under the prevailing pressure below that of the body of hydrocarbons.

5. The process of distilling hydrocarbons for the pyrogenesis of lower boiling point hydrocarbons which consist

in maintaining a body of the hydrocarbons treated in a receptacle under superatmospheric pressure, flowing a stream of such hydrocarbons through a heated zone to said receptacle, cooling the vapors evolved to condense their heavier constituents, and supplying this condensate to said flowing stream.

6. The method of decomposing hydrocarbons for the pyrogenesis of lower boiling point hydrocarbons, which consists in maintaining a body of hydrocarbons treated in liquid state in a receptacle under superatmospheric pressure, flowing a stream of such hydrocarbons through a heated zone to said receptacle effecting a separation for the treated hydrocarbons subsequent to their passage through the heated zone of constituents intermediate between the hydrocarbons treated and the desired low boiling products and supplying the intermediate constituents to said flowing stream.

William M. Burton, Edgar M. Clark.

In presence of J. D. Roop, A. J. Schwartz.

4742

[Vol. 1315]

PETITIONER'S EXHIBIT 196

July 3, 1923 1,461,017

J. H. ADAMS

APPARATUS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS

Filed Dec. 5, 1917 3 Sheets-Sheet 1

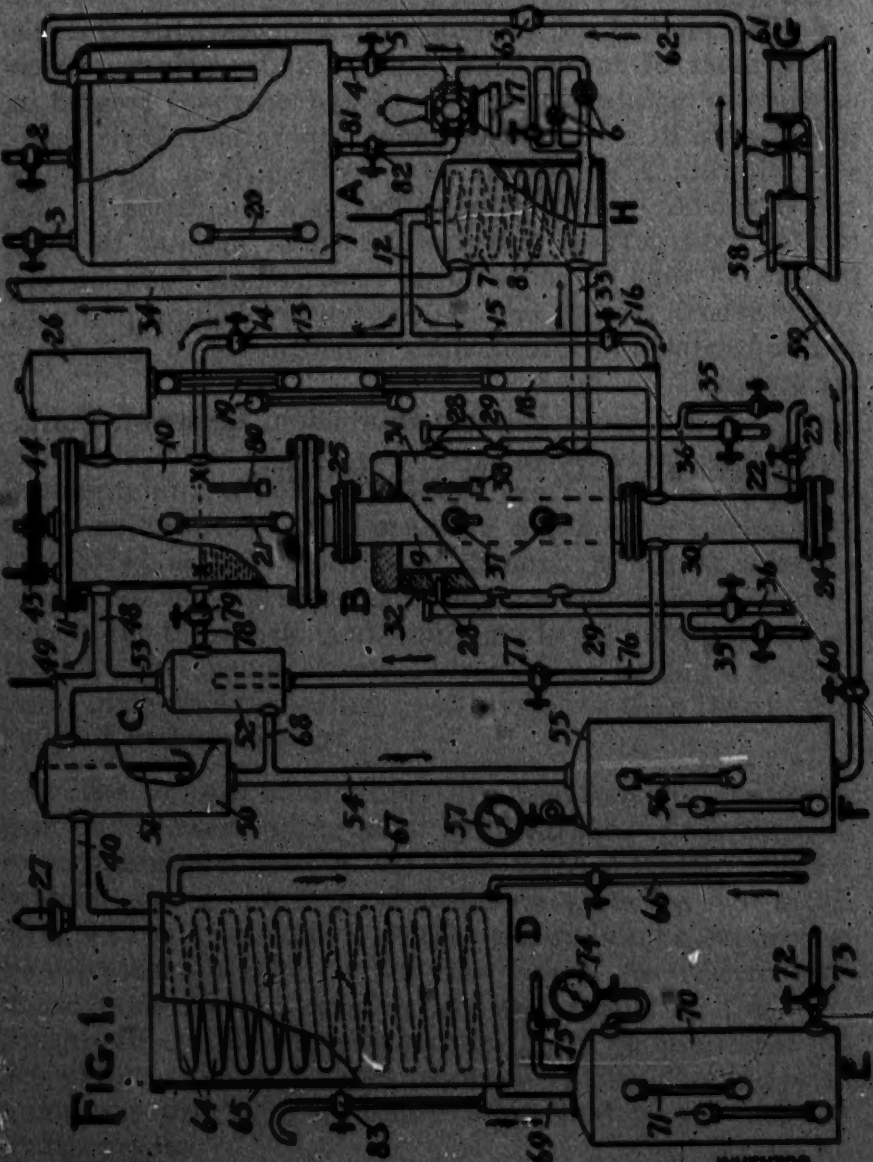


FIG. 1.

WITNESSES:

INVENTOR

ATTORNEYS

PX 196-1

[fol. 1316]

July 3, 1923. 1,461,017

J. H. ADAMS

APPARATUS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS

Filed Dec. 1917 3 Sheets-Sheet 2

FIG. 2.

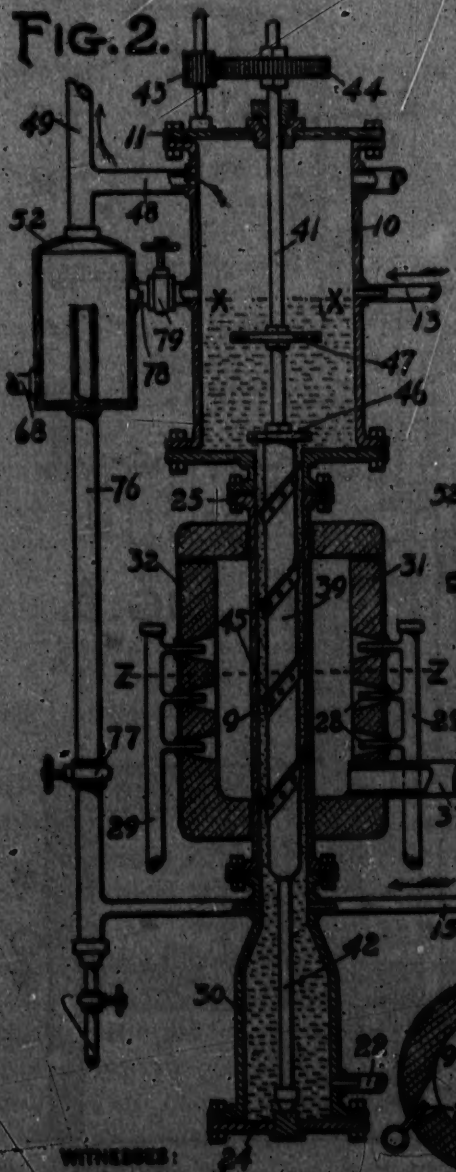
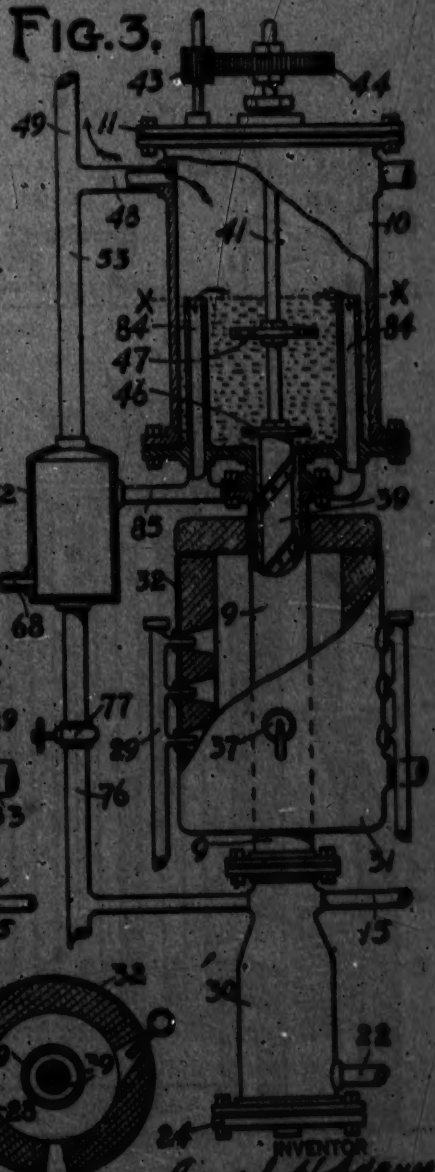


FIG. 3.



WITNESSES:

Justin Adams

Joel Sidebotham

FIG. 4.

INVENTOR

Joseph H. Adams

ATTORNEYS

4744

[fol. 1317]

July 3, 1923. 1,461,017

J. H. ADAMS

APPARATUS FOR THE CONVERSION AND TRANSFORMATION OF LIQUIDS, FLUIDS, AND OILS

Filed Dec. 8, 1917 3 Sheets-Sheet

FIG. 5.

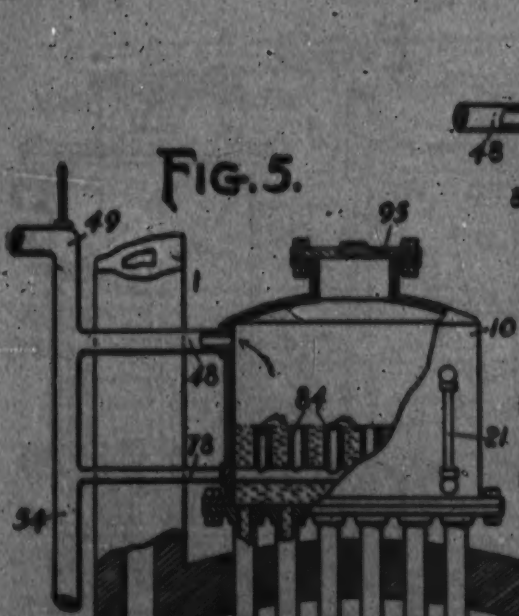
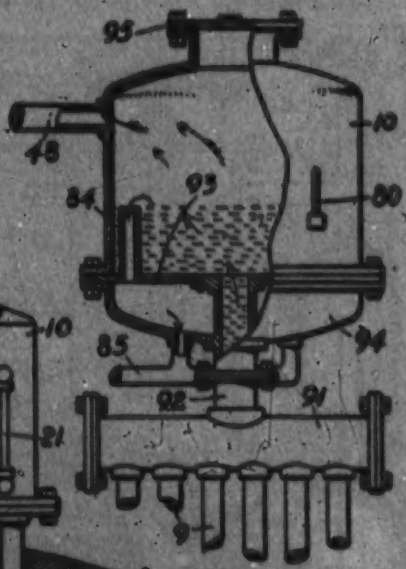
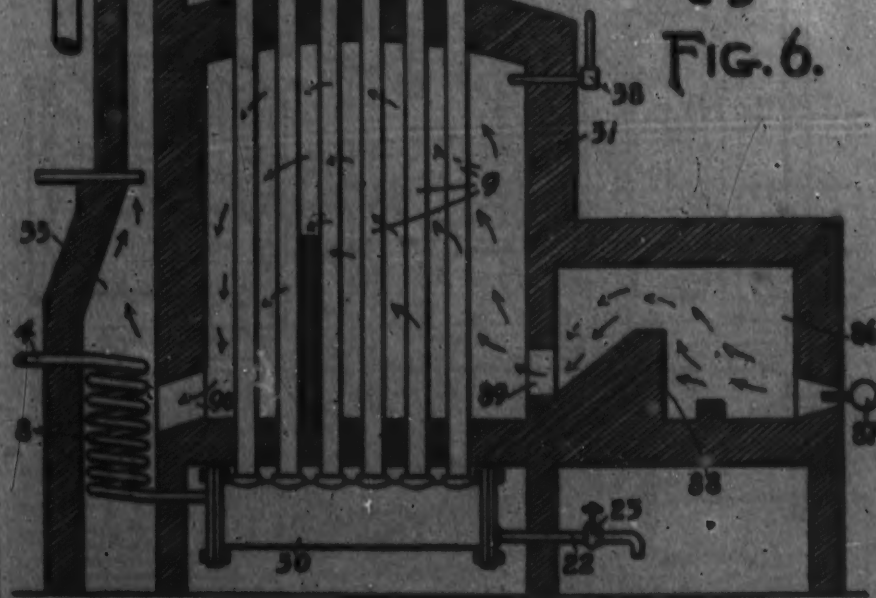


FIG. 6.





WITNESSES:

INVENTOR

ATTORNEYS

[fol. 1318] Patented July 3, 1923. 1,461,017

United States Patent Office

Joseph H. Adams, of Flatbush, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Apparatus for the Conversion and Transformation of Liquids, Fluids, and Oils

Application Filed December 5, 1917. Serial No. 205,528.

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Flatbush, in the county of Kings and State of New York, have invented a new and useful Apparatus for the Conversion and Transformation of Liquids, Fluids, and Oils, and of which the following is a specification.

This invention relates to an apparatus for converting fluids, such as oils, into products of dissimilar character in the manner disclosed and claimed in my co-pending application Ser. No. 618,011, filed March 30, 1911, of which this application is a continuation in part, relating to process as disclosed in my former application Ser. No. 535,879, filed December 31, 1909, which applications have matured into Patent No. 1,327,263, issued January 6, 1920.

One object of this invention is to provide a relatively simple and inexpensive means of externally applying oil cracking heats under easy control to oil contained in tubes and chambers while held under super-atmospheric vapor pressures for the purpose of altering their physical and chemical characteristics to a predetermined extent.

Another object within the contemplation of this invention is to devise an apparatus which will not only facilitate the conversion of heavy oils, such as kerosene distillates, gas oil and other inexpensive hydro-carbons as well as coal tar oils, into lighter oils, such as gasolenes, naphthas, benzol and the like, but will also do so under conditions eliminating the possibility of undesirable interruptions in the continuous process of oil transformation.

This invention seeks to provide an apparatus particularly adapted for "cracking" oils according to my process referred to which, from an operative standpoint, will, in practical usage, possess a high degree of efficiency and durability, and which, structurally considered, will be of the greatest possible simplicity.

Other objects and advantages will be in part obvious from the annexed drawings and the part pointed out in the following description.

The invention accordingly consists in the features of construction, combination of elements and arrangement of parts which will be exemplified in the construction hereinafter set forth, and the scope of the application of which will be indicated in the following claims.

In order that this invention may be the more fully understood and made comprehensible to others skilled in its relating arts, drawings illustrating the preferred adaptation of my apparatus are appended as a part of this disclosure, and while certain modifications in the controlling features of this invention will be readily deducible from this disclosure, such modifications are to be understood as embodied within the intended scope of my appended claims.

In the drawings corresponding parts are similarly referred to by like characters of reference throughout the several views of which:

Fig. 1 is an assembly in elevation showing the several correlated parts of my apparatus as organized for commercially carrying out my process.

Fig. 2 is a sectional elevation on an enlarged scale of the converter showing the cracking tube, the high temperature furnace and the displacement core within the tube.

Fig. 3 is a part sectional elevation of the converter having a larger liquid and vapor separating dome and a modified unconverted oil overflow system.

Fig. 4 is a horizontal section taken through line Z—Z of Fig. 2.

Fig. 5 is a sectional elevation of a multitubular converter having a common header at the lower ends of the tubes and a common liquid and vapor separating dome at the top and:

Fig. 6 shows a modified form of apparatus, as in Fig. 5, with a common header at the top of a multi-tubular con-

verter leading to a liquid and vapor separating dome.

This invention, being of a comparatively simple nature, may be well understood by describing the various features thereof in conjunction with the sequence in which the oil will course through the various parts.

Referring now to Fig. 1, A, represents a suitable tank which serves as a source of oil. It will, of course, be understood that this oil supply apparatus may be arranged in different ways, but that shown on the drawing will be found convenient in ordinary usage.

[fol. 1319] In this embodiment, the containing vessel 1, of the supply apparatus A, may be somewhat elevated with respect to the adjacent converter B, so that the gravitating tendency of the oil may augment its flow into the converter B, under the influence of the more or less weight of oil in the tank and the pressure which may be maintained over it notwithstanding the compression which may be maintained over the surface of the oil in the converter.

The fluid oil may be admitted into the containing vessel or tank 1, by means of a suitable supply pipe indicated by 2, while at the same time the displaced air may escape through pipe 3, from the top of the tank, or pipe 3, may be connected to a suitable air compressor so that a pressure in excess of atmospheric may be maintained over the surface of oil contained therein to further augment the flow of oil from the tank to the converter B.

Such supply tank may be provided with a suitable sight glass gauge 20, in order to observe the height of oil therein and a discharge pipe 4, controlled by valve 5, through which oil may flow to the converter. The pipe connecting tank 1, with oil preheater H, is provided with several precision valves 6, to properly and precisely govern the flow of oil through the heater H, to the converter B, as shown.

For obvious reasons it is best to heat the oil before it is admitted to the converter B, so that the heat from the furnace of the converter may be conserved for the more important function of cracking, splitting the molecules of or rearranging them, and rapidly vaporizing the oil, and therefore the oil heater H, is provided in which the oil may be brought to any desired temperature within the container 7 and tubes 8, by applied heat, the waste heat from the converter furnace 31, the overflow hot oil from the

lower part of dome 10 or by any other economical means of heating.

The oil heater H, and precision valves 6, are placed in the piping system between the source of supply of oil in tank 1, and the converter B, so that the flow of oil may be controlled and heated before entering the converter B.

The figures of the drawing show several of the many diverse forms which the converter may assume within the contemplation of this invention, and the converter shown in Fig. 1, comprises a chamber 9, of heat enduring material and an overlying covered containing vessel of liquid and vapor separating dome 10, closed at the top, by means of cap 11. The supply pipes 4 and 12, lead the oil to pipes 13 and 15, governed by valves 14 and 16, through either one of which oil is admitted to the chamber 9, or lower part of dome 10.

These sections, that is the chamber 9 and dome 10, may be connected with the gauge column 18, on which glass sight gauges 19, are arranged so that the condition and disposition of the contents of the converter may always be the more readily apparent and be susceptible of an intelligent variation by operating the precision valves 6, for regulating the flow of original oil through pipe 4 and preheater H, into the converter B.

The liquid and vapor dome 10, may also be provided with a glass gauge 21, for comparative observation. At the lower part of the converter B, and connected to the cracking tube or chamber 9, a heavy bottoms and residue chamber 30, is arranged to collect the precipitated carbon and foreign substances thrown down in this apparatus by the converting process and near the lower end of this chamber a suitable drip or draw off pipe 22, is located and controlled by the valve 23.

The bottom of chamber 30, is closed by a plate 24, which, as necessity requires, may be removed when cleaning this chamber of carbon and other sediment which may accumulate therein.

The closed containing vessel or vapor dome 10, is secured to the heat enduring or cracking chamber 9, by means of a suitable interposed flange member 25, which is securely bolted to each of these respective sections. Inasmuch as the vapors rising in and filling the upper part of

the vapor dome 10, may, at any time be so rapidly evolved as to exert an undue pressure in excess of the predetermined super-atmospheric vapor pressure under which the apparatus is working, I have arranged an expansion tank 26, on one side of the dome 10, and a release pop valve 27, in the vapor line 40, directly over condenser D, so that any sudden pressure above a given number of pounds per square inch will cause the spring check in the seat of the valve 27, to rise and release the excessive pressure.

It is to be understood that the fittings are made up as tightly as possible and, therefore, I have used between the several flanges, caps and plate gaskets of asbestos and other heat resisting and, indestructible materials, so that the possibility of leakage may be obviated so far as it will be necessary from a practical standpoint.

A feature of primary importance is the means for externally applying heat of intense or cracking temperatures to the oil while contained in the heat enduring chamber 9, while the oil is held under superatmospheric vapor pressures for the purpose of bringing about a conversion of such oil. Preferably this feature is operated by gas and air blast or fuel oil under pressure atomized by steam or compressed air and comprises one or more jets 28, supplied through pipe 29, through which a proper mixture of [fol. 1320] gas and air or oil and steam or compressed air is forced and ignited to form the necessary elements of combustion.

The nozzles of these jets are projected through openings or ports into the furnace 31, composed of fire brick or other refractory material held together within a strong and suitable metallic shell 32, as more clearly shown in Figs. 2, 3 and 4, and provided with an exhaust pipe or stack 33, which may lead the heat and spent gases of combustion to and through the preheater H, then out through pipe 34. The furnace 31 surrounds the converter intermediate its ends, thus insuring that the lower end or bottoms chamber shall be maintained relatively cool for the reception of the heavy residue including the gravitated carbon.

This furnace is designed to conserve the greater part of the intense heat from the several fuel jets 28, for the purpose of maintaining the walls of the heat enduring chamber 9, at a high temperature of sufficient variable intensity while oil is contained within the chamber, in ac-

cordance with the varying characteristics of the oils which may be treated by and according to my process referred to.

In the form shown this furnace 31, with its intake pipes 35 and 36, and outlet or exhaust pipe 33, is made up in cylindrical form to enclose the greater part of the cylindrical heat enduring chamber 9, intermediate its ends and, while this precise form may be varied to conform to the different shapes and designs in which retorts can be made commercially available for this purpose, the form shown in Figs. 1, 2 and 3, will be found very suitable for converting many classes of petroleum and other hydro-carbon oils.

This furnace 31, and heat enduring chamber 9, are especially adapted for the economical use of a mixture of gas and air or fuel oil and air under pressure as an intense heating fuel, and while this unit B, is but one form of converter a number of such units in series would possess commercial advantages. The gas and air being brought in separately through pipes 35 and 36, become mixed within the pipe 29, leading to the jets 28.

When this combustible mixture is ignited the heat action within the furnace 31, may be observed through the sight ports 37, located in the front wall thereof, and the temperature indicated by the pyrometer 38, located in a central position on the furnace where the thermal couple may extend into the body of the generated heat within the enclosure.

For the preservation of the heat enduring chamber 9, and the distribution of heat generated within the walls of the furnace 31, the jets 28, are arranged to enter the ports in the walls of the furnace at a tangent whereby a circulating heat may be distributed about the exterior walls of the chamber 9, as indicated in Fig. 4, instead of the jets being projected directly at local parts of the cracking chamber 9, with chances of possible destruction in a short time.

This form of intense heater is especially adapted for working in the oil and gas regions where the cost of natural gas is very low or the gas manufactured in gas producer plants and fuel oil is inexpensive; or where cheap gas is not obtainable then the form of heater may be changed to conform to the available fuel or means of heat generation to carry on the process in this apparatus.

The oil containing and cracking chamber 9, may be constructed of various heat enduring metals, alloys, carbons, graphites, graphitic carbon and other materials known to withstand a constant and varying temperature, but for the temperatures and super-atmospheric pressures employed in successfully carrying on my process in this form of apparatus, the cold or hot drawn seamless steel tubing having a small porcentage of nickel has proven to be the best for this purpose and to have the greatest enduring qualities when brought to a high or cracking temperature by the application of external heat to it while containing oil.

This intense externally applied heat affects the contained oil in such a manner as to very effectually convert the same and is thus adapted to assist in a step of primary importance as a means in carrying on my process in this apparatus.

It may here be stated that when operating upon certain classes of oils, that is the more volatile oils and oily spirits, it is highly desirable to localize the application of the external heat so as to prevent the spread, so to speak, of the heat in a lower degree of intensity through the mass than is necessary to efficiency "crack" the oil, but of a sufficient intensity to cause an evaporation of undue amounts of the oil at a distance from the intensely heated walls of the cracking chamber without bringing about a transformation.

To this end, in the embodiment of the apparatus shown by Fig. 2, I have provided a cylindrical core or sheath 39, of a size designed to fill a large part of the central space within the cracking chamber 9, and to displace a considerable amount of oil which would otherwise be contained therein, thereby compelling such oil as may be located between this core 39 and the containing chamber 9, to come into more or less direct contact with the intensely heated walls of the cracking chamber 9.

This core 39, is supported by the rods 41 and 42, the whole forming a shaft which by means of a bearing in [fol. 1321] plate 24, at the bottom of heavy bottoms chamber 30, and a packed bearing or gland in the vapor dome cap 11, may be caused to revolve when the gears 43 and 44, arranged above the crown of the vapor dome 10, are operated by power.

A helical collar or worm 45, of metal or other suitable material is attached to the periphery of the core 39, but in such a manner as not to directly engage the interior surfaces of the cracking chamber 9. This core cylinder and collar, when revolving, agitates the oil contained within the cracking chamber 9, and causes it to be thrown into more or less close proximity to the intensely heated walls of the chamber for the purpose of cracking, splitting the molecules of or re-arranging the series and otherwise converting all or as much of the original oil as may be possible during the accelerated movements within and passage through the chamber.

The helical collar 45 has another very important function in preventing an accumulation of particles of carbon, scales and coke which may adhere to or be deposited upon the interior surfaces or walls of the cracking chamber 9 during the cracking operation. In this respect, the helical collar 45 acts as a scraper to positively remove the carbon and other matters from the converter walls whereupon it is permitted to settle or gravitate out of the heating zone and into the relatively cool bottoms chamber 30, from which it may be drawn off through the pipe 22 as desired. In this way an excessive accumulation of carbon on the converter walls is prevented thereby avoiding the building up of a heat insulating coating which soon results in burning out the converter wall. Moreover, the removal of the carbon prevents a progressive accumulation which would tend gradually to choke the system and finally to clog it to such an extent as to interrupt the operation. The helical collar or scraper, therefore, performs a highly important function which permits the apparatus to be operated and the process to be carried on continuously.

From this it will be understood that whenever the fluid to be converted is admitted to the chamber 9, and containing vessel 10, and brought to the proper and safe level, as indicated by the dotted line X—X, in the dome 10, and also indicated in the glass gauges 19 and 21, it is in a position to be operated upon by the externally applied intense heat which will be maintained within the retort 31, and in close relation to the original oil through the walls of the cracking chamber 9, and which, when evolved as vapors, will be constantly and uniformly replaced by fresh quantities of

untreated and non-converted oil. In other words, the oil contained within the channel between the core 39, and chamber 9, will be held in place by the head weight of oil contained in the lower part of vapor dome 10, in addition to the super-atmospheric vapor pressures maintained over the surface of oil, thus preventing the intense heat from too rapidly volatilizing the small amount of oil in this channel and driving it away from the intensely heated walls of the chamber where it is to be broken up or converted into oils having lower specific gravities and boiling points.

The action of the heat is extremely violent, causing the "cracked" oil to become immediately vaporized and the uprising of this vapor brings about a furious local agitation within the cracking chamber 9, and the contained oil.

In order to prevent excessive agitation and "cracking" as known in the present methods of fractional distillation by particles of oil being projected above the body of fluid in liquid and vapor dome 10, and allowing them to drop back again into the heated mass and thereby causing a deteriorating re-action, perforated baffle plates 46 and 47, are located on the rod or shaft and made fast so that they occupy a position within the body of oil, as shown in Figs. 2 and 3.

It may also be mentioned that owing to the excessive quantity of heat, and owing also to the fact that much of the heat will radiate at a diminished temperature into surrounding portions of the oil more distant from the intensely heated walls of the cracking chamber 9, considerable oil may and will be volatized without undergoing conversion, just as illuminating oils and naphthas are boiled and vaporized without essential conversion in the ordinary process of fractional distillation.

By this apparatus under pressure, however, I am able to reduce the undesirable volatization without conversion, to a minimum, and as a consequence the oils are in a large proportion "cracked" or otherwise converted in character. Oil will be constantly flowing toward and into contact with the heated walls of the cracking chamber 9, to take the place of that already vaporized. This newly admitted oil will in turn be "cracked" and changed in the apparatus

into lighter or more volatile products having lower boiling points and specific gravities.

Thus, the complex mixture of oils, known commercially as "distillates" of benzine, kerosene, gas and fuel oils, also coal tar oils may be changed or transformed by means of this apparatus into a mixture of lighter oils and oily spirits which bear a general resemblance to and have the properties of that which is known as illuminating oil, [fol. 1322] naphtha, gasolene, benzol toluol and other low boiling products of the hydro-carbon group.

It may be mentioned also that during this operation, the raw, non-converted oils will be relieved of more or less of the carbon of which they are in part composed, as well as some of the foreign substances which it may be desirable to eliminate. This of course, alters their chemical character and converts them from one or more of the products of the hydro-carbon series into those of lower specific gravity and possible different character. The carbon which is removed in this manner will be in part deposited upon the hot walls of the cracking chamber 9, and in part precipitated in the adjacent oil, being to some extent held in suspension and to some extent gravitating through the oil toward the heavy bottoms chamber 30, provided for its accumulation, and from which it may be withdrawn through the pipe 22.

Inasmuch as the precise degree of temperature at which the walls of the cracking chamber 9, should be maintained in practice, will largely depend upon and be varied with particular conditions, such as the composition of the raw oil to be converted, it will be sufficient to state that the temperature will vary from a heat in excess of that required to merely volatize the oil held under super-atmospheric vapor pressure to that of sufficient intensity to crack and transform the heaviest molecules of an oil subjected to my cracking process referred to in this apparatus, according to the nature of the fluid to be treated.

For practical purposes, however, when treating such oils as kerosene distillates, gas oil and other non-viscous oils a temperature ranging from 600 to 1000° F. would, under super-atmospheric vapor pressures not exceeding 200 pounds to the square inch, bring about the desired transformation of an original high boiling oil into lower boiling

products. When operating in this manner it has been observed that apparently only a certain part of the fluid ultimately evaporated comes in direct or close contact with the intensely heated walls of the cracking chamber 9, for the reason that the condition of the heat is sufficient to evaporate a certain somewhat remote portion of the oil at a lower temperature than is required for "cracking" the oil. Accordingly, the vapors passing into the dome 10, will be composed not only of the oil which has suffered a breaking up of its molecules and deposition of a part of its carbon by the high converting heat, but will also contain a certain portion of unchanged original oil in the form of vapor.

These mixed vapors are evolved very rapidly owing to the intense temperature of the cracking chamber 9, and consequently care should be exercised to keep the oil line in the dome 10, at the proper mark in the glass sight gauges and not permit it to fall below or approach a line which borders on or approaches near to the intensely heated walls of the cracking chamber and which might be followed by searing or burning the oil or discoloring it for commercial purposes.

The mixed vapors pass from the dome 10, into vapor discharge pipe 48, and thence through pipe 49, to a vapor trap 50, of the liquid and vapor trapping system C, in which a baffle plate 51, is arranged in such a manner as to make it necessary for the light vapors to descend nearly to the bottom of the trap on one side of the plate and rise again on the other before they can escape through the gooseneck 40, to the condensing apparatus D.

Vapors not light enough to rise in pipe 49, are condensed then conducted to a liquid trap 52, through the pipe 53, and in like manner vapors not light enough to rise in the vapor trap 50, after descending along the baffle plate 51, fall to the bottom of trap 50, and the condensate is led through pipe 54, into the receiving tank 55, of overflow liquid collecting apparatus F, which latter is provided with glass sight gauges 56, and a pressure gauge 57, and from which the liquid oil may be withdrawn and returned to the supply tank 1, by means of the suction pump 58, of apparatus G, and the pipe 59, controlled by valve 60.

By means of the pump operating mechanism 61, the oil is conveyed through return pie 62, in which the check valve 63, is located to relieve the back pressure on the pump, and finally the oil is admitted through the top of tank 1, as the original oil was let in through pipe 2.

The lighter mixed vapors pass from the trap 50, through the gooseneck 40, and into a suitable condenser coil of pipe 64, immersed in water in tank 65, forming a part of the condensing apparatus D, of Fig. 1. This apparatus D, is provided with a cold water supply pipe 66, and an overflow pipe 67, whereby a continuous flow of cold water can be maintained within the tank 65, for the purpose of bringing about a complete condensation of vapors passing through the coils of pipe 64.

Since some of the vaporized original unconverted oil may tend to condense before reaching the condensing apparatus D, I prefer to connect the bottom of pipe 53, with the liquid trap 52, so that condensate may be led through pipe 68, into pipe 54, the upper end of which is in turn connected with the bottom of vapor trap 50, so that all condensate not accumulated through condensing apparatus D, may be returned to tank 1, after it is collected in receiving [fol. 1323] tank 55, or apparatus F. In this manner the already-condensed unconverted oil may be passed into the cracking chamber 9, again, without first being mixed with and separated from the converted condensed oils in apparatus D, by a fractional distillation method.

After passing through the coil condenser and cooling tank apparatus D, the fluid oil passes through pipe 69, into the apparatus E, of which tank 70, provided with glass gauges 71, is the container and from which it can be withdrawn by means of pipe 72, controlled by valve 73, as shown in Fig. 1. The upper part of this reservoir 70, is provided with a pressure gauge 74, and a gas outlet pipe 75, controlled by a needle valve so that the vapor pressures in the system may be accurately controlled in order to keep a predetermined uniform vapor pressure in the system during the process in this apparatus.

For the treatment of certain oils it is necessary to maintain a super-atmospheric vapor pressure of one or more atmospheres in the apparatus from the source of supply through to the end of or beyond the condenser in conjunc-

tion with the other features of my invention, for thereby I am enabled to retard to a certain extent the over-production of vapors and the volatization of oil that must necessarily be held back and in check within the cracking chamber 9, until as much of the "cracking" operation can be performed on the contained fluid as experience and practice warrants. Furthermore, the vapor compression in connection with the treatment of certain oils will promote uniformity and certainty in the satisfactory operation of the apparatus and, therefore, the compression in addition to normal atmosphere pressure becomes an important feature in the operation of this apparatus for oil transformation.

Thus, from practical experience, it has been found that a super-atmospheric vapor pressure maintained over a body of oil contained in the converter retards the vigorous volatization of the lighter vapors in a desirable manner, assists in the conversion of oil and renders a more uniform flow of product therefrom. On the other hand a greater vapor pressure maintained over a body of oil contained within the converter and throughout the system from the source of supply to the end of or beyond the condenser when treating and converting high boiling oils helps materially in the process of conversion in this apparatus.

The composite oil withdrawn from tank 70, may either be returned to the converter in order to still further convert the same into lighter products, or it may be subjected to fractional distillation or other operations to more or less completely segregate its components, and such components as may not be of the desired quality may then be returned to the converter for further treatment.

When treating oils of different gravities, it may be desirable to cause them to flow either upwardly or downwardly through the cracking chamber 9, and for this purpose intake pipes 13 and 15, are provided. When fluid is admitted through the lower part of apparatus B, valve 14 in pipe 13, and valve 77 in pipe 76, is closed. Valve 16 in pipe 15, and valve 79 in pipe 78, is opened thereby allowing the oil to flow through pipe 15, into the lower part of the converter. By the continuous method of supply and discharge, the unconverted oil which has not been driven off in vaporous form flows out through pipe 78, into liquid

trap 52, then through pipe 68, into pipe 54 and down into collecting tank 55. With this arrangement, the pipe 78 serves as an overflow for the oil supplied to the converter and maintains the oil level therein substantially constant throughout the operation.

When oil is admitted to the upper part of converter B, through pipe 13, valve 16 in pipe 15, and valve 79 in pipe 78, is closed and valve 77 in pipe 76, is opened. The head weight and pressure on the oil in the lower part of vapor dome 10, causes the oil to flow down through cracking chamber 9, and out through pipe 76. It is then forced up through the pipe 76, (Figs. 1 and 2) and over into liquid trap 52, and flows out through pipe 68, into pipe 54, from which it is discharged into tank 55.

For the purpose of determining the proper speed at which the oil should flow through converter B, a pyrometer 80, is located near the lower external part of the liquid and vapor dome 10, so that when the proper speed of flow has been established this pyrometer will register a uniform temperature in the oil when it is passing through the converting chamber 9, in an upwardly direction.

For the purpose of maintaining a positive feed of continuously flowing oil from supply tank 1, through the preheater H, into the converter B, a pump 17, is interposed in the piping system and by closing valve 5, in pipe 4 and opening valve 82, in pipe 81, and operating this pump a constant and positive flow of oil will be assured to the converter.

In order to be informed of the temperature of oil being fed from the preheater H, into the converter B, a thermometer is located in the pipe 12, leading out from the top of the heater, and in pipe 49, leading out from the top of the converter B, another thermometer is located so that temperatures of the converted oily vapors may be known.

An emergency gas outlet is provided in the pipe 69, leading from the foot of the condensing apparatus D, and is [fol. 1324] controlled by valve 83. Such valve, however, is but little used since the more efficient and better located pipe and control valve 75, on the top of tank 70, will answer about every purpose for properly regulating vapor pressures within the system.

In Fig. 2, an enlarged sectional elevation of the converter is shown and the described features of the various parts are clearly illustrated. In Fig. 3, a somewhat similar view is shown of a converter where a larger liquid and vapor dome is employed having overflow pipes 84 located at the lower part of the dome through which overflow hot unconverted oil may pass into trap tank 52, through pipe 85. A substantially constant oil level is thereby maintained.

In this form of converter oil is supplied through the lower pipe 15 only. The converted vapors pass off from the top of dome 10, through pipe 48, to the condenser while partly or wholly unconverted oils will overflow the pipes 84, and can be returned to the supply tank 1, for re-treatment as before.

A number of pipes 84, arranged at the bottom of dome 10, will facilitate the rise and escape of light vapors which may not have had time to separate from the oil at the surface level X—X, due to its continuous and more or less rapid flow through the converter.

In Fig. 5, the same principle of vertical tubes and externally applied heat is carried out in this multi-tubular converter in which the chambers 9, are enclosed within the furnace 31. This form of furnace is provided with a combustion chamber 86, into which the elements of combustion are projected by means of burners or jets 87, which elements as they ignite and expand, are deflected by the bridge wall 88, before entering the larger furnace 31, through port 89 The waste heat and spent gases from furnace 31 pass out through port 90, into stack 33, and in their passage, such heat is employed to preheat incoming oil through pipe 4, in the coils 8, before being delivered into the upper part of heavy bottoms chamber 30.

As described in the reference to Fig. 1, the oil becoming converted in the tubes 9, rise and the light transformed vapors therefrom escape from the upper part of liquid and vapor dome 10, through pipes 48 and 49, to the condenser D, while the heavier partly or wholly unconverted oils overflow the pipes 84, at a fixed level and flow through pipe 78, to pipe 54, where they are trapped in tank 55, and returned to tank 1, for retreatment together with fresh oil.

In Fig. 6, a modified upper part of the converter and dome are shown where the upper ends of the chambers 9, take into a header 91, from which the oil and vapors rise into

dome 10, through a neck 92. An inner bottom 93, is arranged near the lower part of this dome 10, and the oil flowing up through neck pipe 92, rises to the fixed height of the stand pipes 84, over and down through which it flows into the cavity or well 94, and is led out through pipe 85, to the liquid trap 55, to be in turn re-treated.

The object of this improved dome is to facilitate the better separation of converted vapors from unconverted oils and which vapor may rise through the stand pipes 84, as the liquid overflows and escapes through pipe 48, to the condenser where, under the vapor pressure in excess of atmospheric pressure, the condensable vapors are reduced to condensate or distillate of converted oils. A man hole plate 95, can be attached to the top of this dome 10, so that access can be had to the interior of such dome, when necessary.

The above specifically described apparatus may, of course, be modified greatly and yet be well within the scope of a co-related system composed of parts adapted to carry out one or more of the essential closely related steps of my process.

It is apparent that I have succeeded in devising an apparatus admirably adapted for carrying out my new method of commercially enhancing the quality, quantity and value of the more abundantly available oils and that the character of the apparatus and of the process which it is instrumental in carrying out are both within the usual manipulative skill of those employed in this art. As many changes could be made in the above construction and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limited sense.

It is also to be understood that the language used in the following claims is intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

Claims

1. In a device of the class described the combination of an elongated vertical chamber adapted to contain oil and

vapors under pressure, means for supplying oil to said chamber, means for externally heating said chamber above its bottom and below its top, means for removing carbon from said chamber below the heating zone, means for removing vapors and unconverted oil from said chamber [fol. 1325] above the heating zone, means for maintaining self-imposed vapor pressure in said chamber and means for condensing the vapors.

2. In a device of the class described the combination of an elongated vertical chamber adapted to contain oil and vapors under pressure, means for supplying oil to said chamber, means for externally heating said chamber above its bottom and below its top, means for removing carbon from said chamber below the heating zone, means for separately removing vapors and unconverted oil from said chamber above the heating zone, means for maintaining self-imposed vapor pressure in said chamber, rotary mechanical means in said chamber for preventing the caking of carbon on the hot surfaces of said heating zone.

3. In a device of the class described the combination of an elongated vertical chamber adapted to contain oil and vapors under pressure, means for supplying oil to said chamber, means for externally heating said chamber above its bottom and below its top, means for removing carbon from said chamber below the heating zone, means for maintaining self-imposed vapor pressure in said chamber, rotary mechanical means in said chamber for preventing the caking of carbon on the hot surfaces of said heating zone, means for separately removing vapors and unconverted material from said chamber above the heating zone, means for separating the converted from the unconverted vapors and means for returning the unconverted material to said chamber for retreatment.

4. In a device of the class described the combination of a receptacle adapted to contain a body of oil and vapors under self-imposed pressure including an enlarged dome or chamber and a portion or restricted cross-section leading to said chamber, means for continuously forcing oil through said restricted portion to said chamber, means for exteriorly heating said oil in said restricted portion to a cracking temperature, means for removing carbon generated in said

heated portion out of the heated zone, and means for drawing off and condensing the vapors in said dome.

5. In a device of the class described the combination of an elongated vertical chamber adapted to contain oil and vapors under pressure, means for externally heating said chamber above the bottom but below the top to a cracking temperature, means for continuously supplying oil under pressure to said chamber, rotary means extending from the top down to said heating zone to prevent collection of carbon, means for separately removing vapors and unconverted oil from the upper portion of said chamber, and means for maintaining self-imposed vapor pressure on the oil in said chamber.

6. In a device of the class described for the conversion and transformation of high boiling hydrocarbons to lower boiling products, the combination of an oil supply tank, a substantially vertical tubular cracking chamber, a high temperature furnace capable of withstanding protracted elevated cracking heats surrounding said chamber, the ends of said tubular chamber extending through the top and bottom of said furnace, a carbon and residue chamber at the lower end of said chamber below the furnace, a liquid and vapor collecting and separating drum connected to the upper end of said chamber, a condenser and a collecting trap tank in open connection with said drum; means for forcing oil from said supply tank into said cracking chamber against a back pressure of vapors therein, means for withdrawing partly or wholly unconverted oil from said drum and returning it to said oil supply tank, and means for maintaining self generated vapor pressure throughout the system from the source of supply through to the end of or beyond the condenser.

7. Apparatus for converting high boiling hydrocarbons into lower boiling hydrocarbons, which comprises a furnace for subjecting the oil to cracking temperature, a vertical converter extending above the furnace at the top and below the furnace at the bottom, means for removing solid matter from the converter, a condenser connected to the converter above the heated zone, and means for closing the system beyond the condenser to permit self-imposed vapor pressure to be built up therein.

8. Apparatus for converting high boiling hydrocarbons into lower boiling hydrocarbons, which comprises a furnace for subjecting the oil to cracking temperature, a vertical converter extending above the furnace at the top and below the furnace at the bottom, a removable bottom therefor, means for maintaining liquid hydrocarbons in the converter above the heated zone, a condenser connected to the converter above the heated zone, and means for closing the system beyond the condenser to permit self-imposed vapor pressure to be built up therein.

9. Apparatus for converting high boiling hydrocarbons into lower boiling hydrocarbons, which comprises a furnace for subjecting the oil to cracking temperature, a vertical converter extending above the furnace at the top and below the furnace at the bottom, means for maintaining liquid hydrocarbons in the converter above the heated zone, a condenser connected to the converter above the heated zone, means for closing the system beyond the condenser, to permit self-imposed vapor pressure to be built up therein, and [fol. 1326] means for removing solid matter from the relatively cool bottom of the chamber.

10. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter, means for continuously passing oil in liquid form to, through and out of said converter, and a furnace enveloping the converter above the lower end for externally heating and oil therein to a cracking temperature under superatmospheric self-imposed vapor pressure whereby a portion of the oil is cracked in transit, the lower end of said chamber being adapted to receive carbon produced during the cracking process.

11. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter means for continuously passing oil in liquid form into said converter, means for discharging liquid oil therefrom at a predetermined height whereby a constant oil level is maintained therein, and a furnace enveloping the converter above its lower end for heating oil therein to a cracking temperature under superatmospheric self-imposed vapor pressure to effect conversion of the oil in transit through the converter.

12. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter, an outlet discharge pipe therefore located at a predetermined height immediate its ends, an inlet pipe communicating with said converter, means for continuously passing liquid oil through said inlet pipe into said converter and, in serving in conjunction with said outlet pipe to maintain a substantially constant oil level therein, a furnace surrounding said converter above its lower end for externally applying cracking heat under super-atmospheric self-imposed vapor pressure to the oil therein, and means for returning to said converter for retreatment the liquid oil discharged therefrom.

13. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter maintained at a cracking temperature and under super-atmospheric self-imposed vapor pressure, means for supplying oil to said converter, means for withdrawing the evolved vapors, positive means for preventing the accumulation of carbon on the walls of the converter in the heating zone, and means disposed below the heating zone for receiving the carbon gravitating therein and means for permitting the removal of solid matter therefrom.

14. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter, means for supplying oil thereto, means for heating the oil intermediate the ends of a converter to a cracking temperature under super-atmospheric self-imposed vapor pressure, means for withdrawing the evolved vapors, means for scraping the walls of the converter in the heating zone to remove carbon deposited thereon during the cracking process, and permitting the removed carbon to gravitate into the lower and relatively cool end of the converter below heating zone, and means for withdrawing the residue including the carbon from the lower end of the converter.

15. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a vertical converter, means for supplying oil continuously thereto, means for heating the oil in the converter to a cracking temperature under super-atmospheric self-imposed

vapor pressure whereby the oil is converted, means for withdrawing the evolved vapors, continuously rotatable means for scraping off the carbon deposited on the walls of the converter during the cracking process and permitting it to gravitate out of the heating zone, a chamber below the heating zone for receiving the gravitated carbon and other residue, and means for removing the same therefrom.

16. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter, means for continuously supplying oil thereto, a furnace enveloping the converter intermediate its ends for heating the oil therein to a cracking temperature under super-atmospheric self-imposed vapor pressure, a rotatable scraping device in proximity to the walls of the converter in the heating zone for preventing the accumulation of carbon thereon during the cracking process and permitting it to continuously gravitate out of the heating zone and into the relatively cool lower end of the converter and means for permitting its removal as desired.

17. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter maintained above its lower end at a cracking temperature and under super-atmospheric self-imposed vapor pressure, means for continuously supplying oil thereto and maintaining a substantially constant oil level therein, means for withdrawing the evolved vapors from the vapor space above the oil level, means for continuously and positively removing the carbon deposited on the walls of the converter in the heating zone and permitting it to gravitate into the lower end of the converter, and a removable bottom for effecting its withdrawal.

18. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a [fol. 1327] converter, means for continuously supplying oil thereto and maintaining a liquid body of oil therein, means surrounding said converter intermediate its ends for heating the converter to cracking temperature under super-atmospheric self-imposed vapor pressure whereby the oil is converted, means disposed in a relatively cool region for receiving carbon produced during the cracking process, and means associated with said carbon receiving means for effecting its removal therefrom.

19. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter maintained at a cracking temperature and under super-atmospheric self-imposed vapor pressure, means for continuously supplying oil thereto and maintaining a liquid body of oil therein, means for continuously removing the carbon deposited on the walls of the converter during the cracking process, means for receiving a removed carbon, and means for withdrawing the residue from said receiving means.

20. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination of a converter, a furnace surrounding the converter intermediate its ends for externally applying a cracking temperature to the oil therein while maintaining the oil under super-atmospheric self-imposed vapor pressure, means for continuously supplying oil thereto and maintaining a liquid level above the heating zone, means below the heating zone for collecting the carbon produced by the cracking process, and means above the heating zone for separately conveying away therefrom the unconverted oil and the converted vapors.

21. In apparatus for converting high boiling hydrocarbon oil into lower boiling products, the combination with an enclosed vertical cracking chamber adapted to contain a body of oil to be converted, means for continously supplying oil to the lower portion of the body of oil in said chamber and to maintain a substantially constant level therein, means for removing unconverted liquid oil at the liquid level, means for for externally heating said chamber intermediate its ends and below the liquid level to a cracking temperature a condenser having free and open communication with the vapor space of said chamber above the liquid level, means for closing the system beyond the condenser to permit self-imposed pressures to build up therein, and means including a scraping device for separating out the carbon produced in the chamber during the cracking operation by scraping carbon from the walls of the chamber as it is deposited thereon and allowing it to gravitate below the cracking zone and be removed.

22. Apparatus for continuously converting high boiling hydrocarbon oil into lower boiling products that comprises

a vertical cracking chamber maintained under super-atmospheric self-imposed vapor pressure, a furnace surrounding the chamber intermediate its ends for heating the oil in the heating zone to a cracking temperature, means for continuously supplying an oil distillate thereto and maintaining a body of oil throughout the length of the heating zone, means for taking off the evolved vapors from the vapor space above the heating zone, and means for positively removing the carbon deposited upon the walls of the chamber within the heating zone and allowing it to gravitate and collect in the lower end of the chamber below the heating zone.

In testimony whereof I affix my signature in the presence of two witnesses.

Joseph H. Adams.

Witnesses: A. Capstick, Joel S. de Selding.

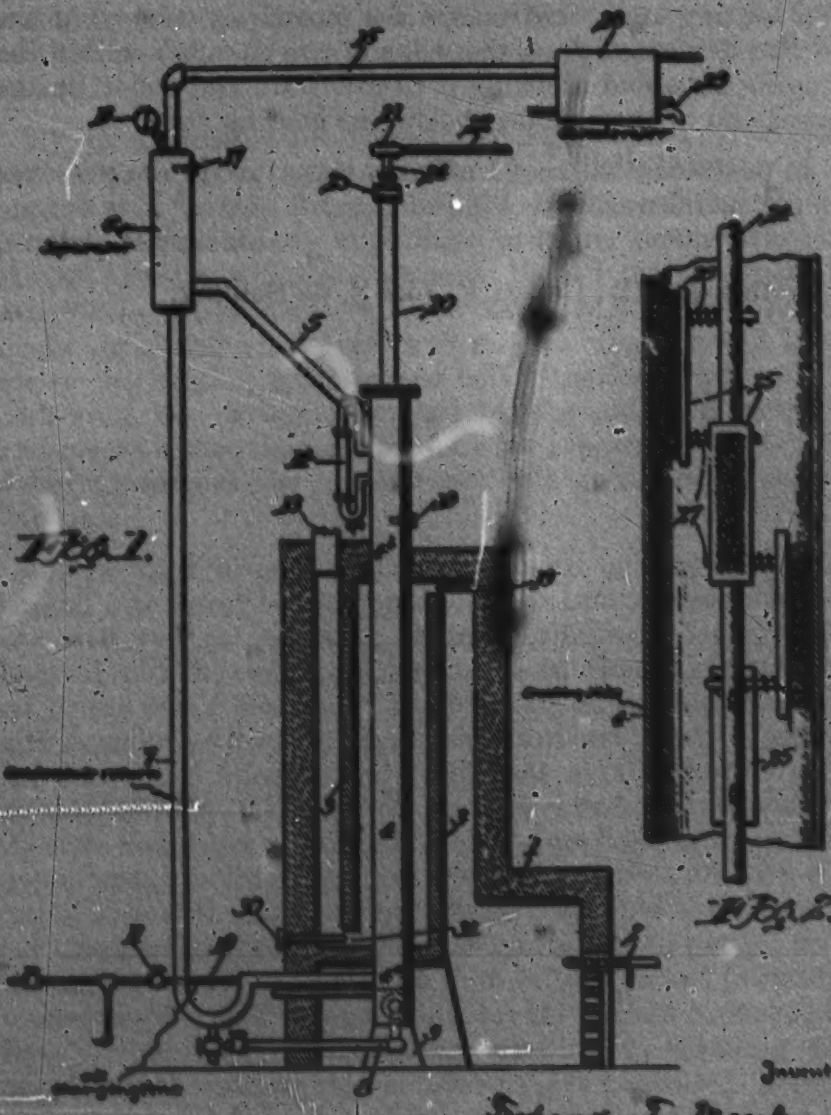
[fol. 1328] PETITIONER'S EXHIBIT 197

July 17, 1923. 1,462,143

F. T. MANLEY

METHOD OF CRACKING HYDROCARBON OILS

Filed Oct. 10, 1917



Inventor

Richard T. Manley

[fol. 1329] Patented July 17, 1923. 1,462,143

United States Patent Office

Frederick T. Manley, of Houston, Texas, Assignor to the Texas Company, of New York, N. Y., a Corporation of Texas

Method of Cracking Hydrocarbon Oils

Application filed October 10, 1917. Serial No. 195,775

To all whom it may concern:

Be it known that I, Frederick T. Manley, a citizen of the United States, residing in Houston, Harris County, and State of Texas, have invented certain new and useful Improvements in Methods of Cracking Hydrocarbon Oils, of which the following is a specification.

This invention relates to novel processes by which higher-boiling hydrocarbons are decomposed or broken up into lower-boiling hydrocarbons. It relates particularly to the cracking of such oils as kerosene, gas oil, lubricating oil, and the like, for the production of more volatile products, such as are usually designated by such terms as gasolene and naphtha. More especially it relates to novel and improved processes by which is effected the decomposition of certain of the more readily volatilized constituents which are formed in cracking the higher-boiling hydrocarbons, and which, although not sufficiently volatile for gasolene or naphtha are yet so readily volatilized that it is difficult under existing practices to hold them within a zone of sufficient heat to decompose them.

In the practice of cracking hydrocarbons for the production of the more volatile products, as gasolene, considerable difficulty has hitherto been experienced in the proper disposal of the large proportion of constituents of the kerosene type usually formed when using the requisite pressures and temperatures needed for cracking the hydrocarbons which it is commonly sought to decompose into gasolene. Attempts have been made to effect a cracking of these constituents by returning them to the still by such methods as the use of inclined vapor lines and traps of various kinds, but the volatility of said constituents is such that upon

coming in contact with the vapor portion of the still they are vaporized by the heat without, however, being heated sufficiently for decomposition. The result is that these constituents of the kerosene type tend to collect in great quantities in the upper portions of the still and in the vapor lines leading therefrom. They are too heavy to be used for the gasolene fractions, yet are so easily volatilized that they do not drop back into a zone of sufficient heat to decompose them into lighter products. As a result of the accumulation of these kerosene constituents the operator is forced to increase the pressures used, thus augmenting the danger, as well as the expense of carrying on the operation. It is an object of this invention to collect these constituents of the kerosene type, return them directly to the bottom of the still into which they are positively forced and retain them there for a sufficient time to decompose them into more volatile products.

Certain novel apparatus for carrying out the herein disclosed process is illustrated in the accompanying drawing, but is not claimed herein as it is made the subject of my co-pending application Serial No. 195,774, filed October 10, 1917.

In the drawings

Figure 1 shows partly in vertical section an apparatus adapted to carry out my invention; and

Figure 2 is an enlarged section of a portion of the cracking tube showing scraping means therein.

Referring to the drawing, a cracking still 4, with suitable supports 9 heated intermediate its ends, is placed in a furnace 1, having baffle walls 3, burner 2 and stack 13. A vapor line 5 extends from the upper portion of the cracking still above the heating zone to an air condenser 6. A return conduit 7 reaches from the air condenser directly to the lower portion of the cracking still 4 below the heating zone in order to return condensed material. 8 is a valved draw-off pipe at the bottom of the cracking still 4.

The still is preferably equipped with a supply pipe 10 entering the horizontal section of the conduit 7 whereby the introduction of the oil charge is caused to produce an injector effect by which the material in the pipe 7 may be forced into the still.

A vapor line 15 extends from the air condenser 6 to suitable water condensers 28. The outlet from the condenser

28 has a valve 29. 16 denotes a pressure gauge on the air condenser to indicate the vapor pressure therein. 17 and 18 designate recording thermometers on the air condenser and cracking still, respectively, and 19 and 30 furnace pyrometers. A gauge 14 for indicating the liquid level in the still 4 is situated at the upper part thereof.

In this form of apparatus the oil in the cracking still 4 [fol. 1330] forms an extended vertical column and the charging oil and condensate forcibly supplied at the bottom, passes up through that column and is thus subjected to the cracking operation. In order to keep the inner surface of the cracking still clean and prevent the collection of material on that surface, I preferably provide a scraping device as shown in detail in Figure 2. The scraping device includes a shaft 24 extending centrally down into the cracking still and engaging any suitable bearing at the bottom. This shaft carries steel brushes 25, the brushes being secured to the shaft by the rods 27, around which are placed coiled springs 26 to yieldingly press the brushes against the inner surface of the still 4. The shaft 24 may be driven through a worm gear 21 from the shaft 22. In order to support the shaft at its upper end I preferably mount a pipe 20 in the upper end of the still 4 slightly larger in diameter than the shaft 24, and at the upper end of this pipe 20 I place a stuffing box 23. The purpose of this pipe 20 is to place the stuffing box in a relatively cool position. The brushes in the still 4 are placed only in the cracking zone which, as illustrated in Figure 1, is between the parts marked 4^a and 4^b.

The heating arrangements of the furnace are such that the hot combustion gases pass upward from the burner 2 between the furnace wall 1 and baffle 3 until they are deflected by the top wall of the furnace into the heating chamber which contains the cracking still and is formed by the baffle 3. The hot gases pass downwardly imparting heat to the cracking still and find exit at 31 to and through the stack 13. The upper and lower ends of the cracking still preferably extend beyond the heating zone.

In the operation of my process, I charge the still 4 with the hydrocarbon oil which it is desired to decompose into lighter products, such as gasolene. The liquid level throughout the operation is maintained at a point above the heating zone in the upper portion of the still. By regulating the

supply of oil entering the still through the charging line 10, hydrocarbon in the cracking still is ordinarily heated to from 650° to 800° F., the exact temperature needed being dependent upon the character of the charge. I maintain and regulate pressure in the apparatus by means of the valve 29, in the condenser outlet. I use a pressure not ordinarily below 100 lbs. and may employ one as high as 300 lbs. The vapors generated pass out from the cracking still through the vapor line 5 to the air condenser 6. The constituents of the desired volatility, that is, ordinarily those of the gasolene or naphtha type, are carried to the water condensers by the conduit 15.

The less volatile constituents, that is, ordinarily predominantly those of the kerosene type are liquefied in the air condenser and dropped down into the return conduit 7 by which said constituents are carried back directly to the cracking still.

The returned condensate is forced in at the bottom of the heated liquid column in the cracking still and by reason of the fact that its boiling point is below the mean boiling point of the contents of the still it tends to vaporize comparatively rapidly thereby creating a current up through the liquid column. This current acts as a carrier of the light hydrocarbons being generated in the cracking operation and serves to remove them from the cracking zone as formed, thus preventing decomposition of the light liquefiable hydrocarbons into permanent gases.

By reason of the extent of the cracking zone the returned condensate is subjected to a cracking temperature for a sufficient time to cause the conversion of substantial portions thereof into the desired volatile products. The operation is cyclic, the heavier condensates collecting in the separator 6 continuously being returned to the cracking still 4 and passed upward through the heated liquid column, thus continuously decomposing these returning constituents into lighter and more volatile products. In this manner the constituents of the kerosene type, which have hitherto been found so difficult to crack, may readily be decomposed into the desired products. By carrying on the cracking in the liquid phase the conversion is effected without heating the hydrocarbons unduly or unevenly thus avoiding undue carbonization and the formation of excessive quantities of gas or of unsaturated compounds.

By continuously returning to the cracking still 4 the condensate collected in the separator 6 the zone of reaction in the cracking still 4 is saturated with hydrocarbons of the kerosene type thus bringing about a chemical equilibrium tending to a reduction in the formation of this type of hydrocarbons and making possible an increased formation of the gasolene products desired.

The tube 7 is insulated so as to prevent undue loss in heat by the products passing through it. By returning these constituents to the heating zone while still in a heated condition a considerable economy is effected in the amount of fuel required to carry on the cracking operation.

The volatile product desired leaves the separator 6 in the form of vapor and is conducted by the vapor line 15 to the condenser 28 wherein the product is condensed, the condensate being withdrawn through the valved outlet 29. The residue collecting in the still may be drawn off as desired through the outlet pipe 8.

It is well known that the character of the products returned to the cracking oil from the air condenser by means [fol. 1331] of the conduit 7 will vary not only with the character of the hydrocarbon oil introduced into the still, but with the temperature and pressures employed, and with other variable factors, as the speed of the operation, so that in the normal operation of the process certain constituents may be returned which may not come strictly within the meaning of the term "kerosene" as that word is commonly employed in the art. But I prefer to use the word "kerosene" herein, since in the normal operation of the process the returned constituents are predominantly those of the kerosene type. It is understood that by means of my process the products generated by the cracking operation, which are less volatile than desired, and which either through the readiness with which they are vaporized, or on account of mechanical action or other cause, pass out from the cracking zone, are continuously and directly returned to the cracking zone and are forced through the heated liquid column so that these constituents are all eventually decomposed into products of the gasolene or naphtha type.

What I claim and desire to secure by Letters Patent is:

1. The continuous method of cracking hydrocarbon oils which comprises charging the oil into an elongated vertical

still to maintain therein an extended column of liquid oil, maintaining said column of oil under temperature and pressure sufficient for cracking, collecting the generated vapors and separating therefrom the less volatile constituents thereof, continuously and directly returning said less volatile constituents and positively forcing them into the bottom of the still so that they are caused to pass through substantially the full length of the extended column of oil therein, and condensing the constituents of desired volatility.

2. The continuous method of cracking hydrocarbon oils which comprises charging the oil into an elongated vertical still to maintain therein an extended column of liquid oil, maintaining said column of oil at a temperature and pressure sufficient for cracking, removing residue and vapors from the still to maintain a substantially constant liquid level therein, separating out the heavier constituents of said vapors and directly returning said constituents in cyclic passage through substantially the full length of the extended column of oil by positively forcing them into the bottom of the still.

3. The continuous method of cracking hydrocarbon oils that comprises charging the oil into the bottom of an elongated vertical still to maintain an extended column of liquid oil therein, maintaining said column of oil under sufficient heat and pressure for cracking, separating out the heavier constituents of the evolved vapors, and directly returning and injecting them with the charging oil into the bottom of the still so that they are caused to pass through substantially the full length of the extended column of oil therein.

4. The continuous method of cracking hydrocarbon oils that comprises charging the oil into a vertical still to maintain therein an extended column of liquid oil, heating said column of oil intermediate the ends of the still to maintain a cracking temperature therein, allowing the generated vapors to collect in the upper end of the still above the portion thereof to which heat is applied, continuously removing the collected carbon formed and causing it to collect at the bottom of the still below the heating zone, controlling the removal of the vapors from the still to maintain therein a superatmospheric pressure, separating out the heavier constituents of the vapors and directly returning

said constituents in cyclic passage through substantially the full length of said column of oil by forcing them together with the charging oil into the bottom of the still.

5. The continuous method of cracking hydrocarbon oils which comprises charging the oil into an elongated vertical still to maintain therein an extended column of liquid oil, maintaining said column of oil under temperature and pressure sufficient for cracking, collecting the generated vapors, cooling said vapors to condense the heavier constituents thereof, preventing further cooling of the resulting condensate and directly returning same in a heated condition and positively forcing it together with the charging oil into the bottom of the still so that the condensate is caused to pass through substantially the full length of the extended column of oil therein.

6. The continuous method of cracking hydrocarbon oils which comprises charging a stream of oil into the bottom of a cracking still to maintain a body of oil therein, maintaining the oil therein under pressure and at a cracking temperature, removing the evolved vapors, separating out the heavier constituents thereof, and returning them directly to the still for further treatment by positively forcing them in the stream of charging oil into the bottom of the still.

7. The continuous method of cracking hydrocarbon oils which comprises charging the oil into an elongated vertical still to maintain an extended column of liquid oil therein, maintaining said column of oil under temperature and pressure sufficient for cracking, collecting the generated vapors separating therefrom the less volatile constituents, and positively forcing them into the bottom of the still so that they are caused to pass through substantially the full length of the extended column of oil therein.

[fol. 1332] 8. The continuous method of cracking hydrocarbon oils which comprises charging the oil into a still to maintain a body of oil therein, subjecting the oil therein to cracking temperature and pressure, removing the evolved vapors, separating out the heavier constituents thereof, and returning them in heated condition in cyclic passage to the still for further treatment by positively forcing them into the bottom of the still.

In testimony whereof I do affix my signature.

Frederick T. Manley.

[fol. 1333] PETITIONER'S EXHIBIT 198

July 24, 1923. 1,462,677

J. H. ADAMS

OIL CONVERTING PROCESS FOR THE CONVERSION AND TRANSFORMATION OF OILS

Filed June 15, 1916 5 Sheets-Sheet 1

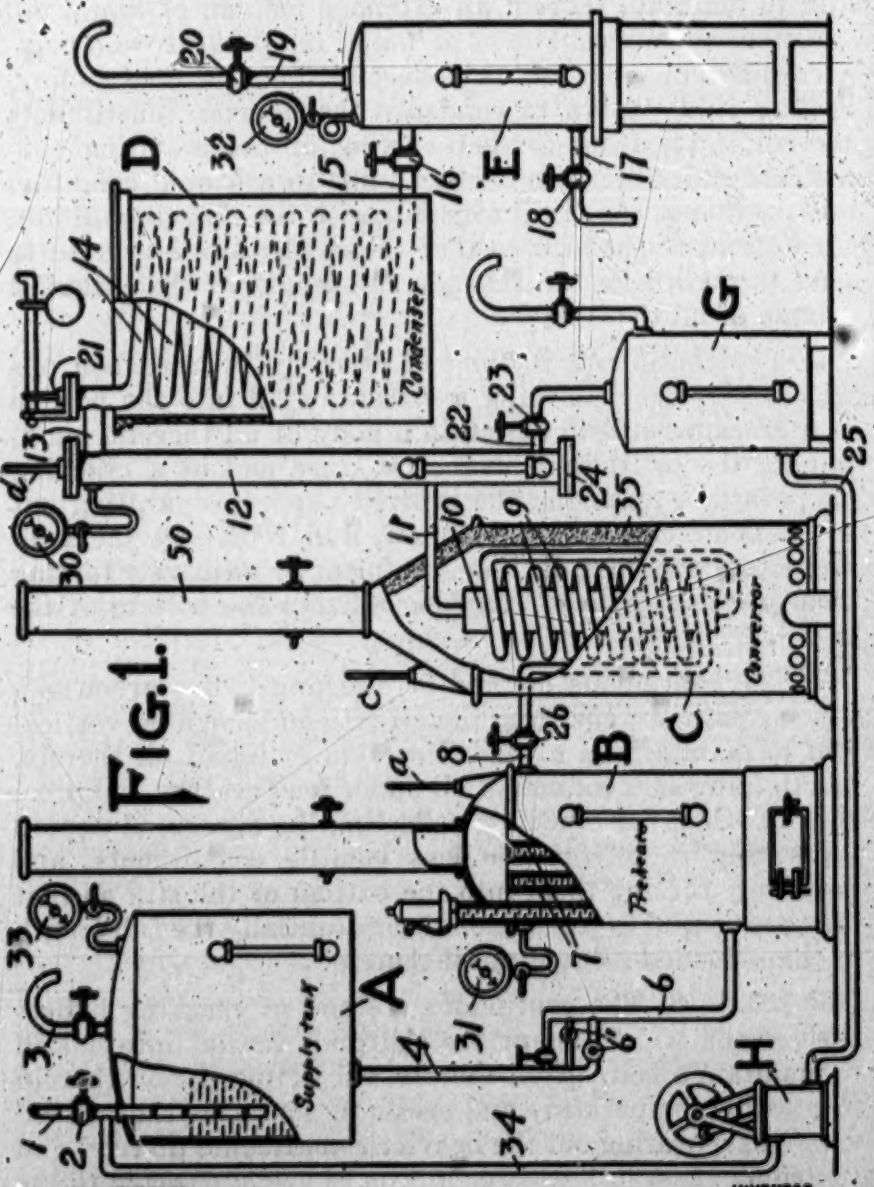


FIG. 1.

WITNESSES:
A. Capstick
Joel Abdelding

INVENTOR
Joseph H. Adams

[fol. 1334]

July 24, 1923, 1,462,677

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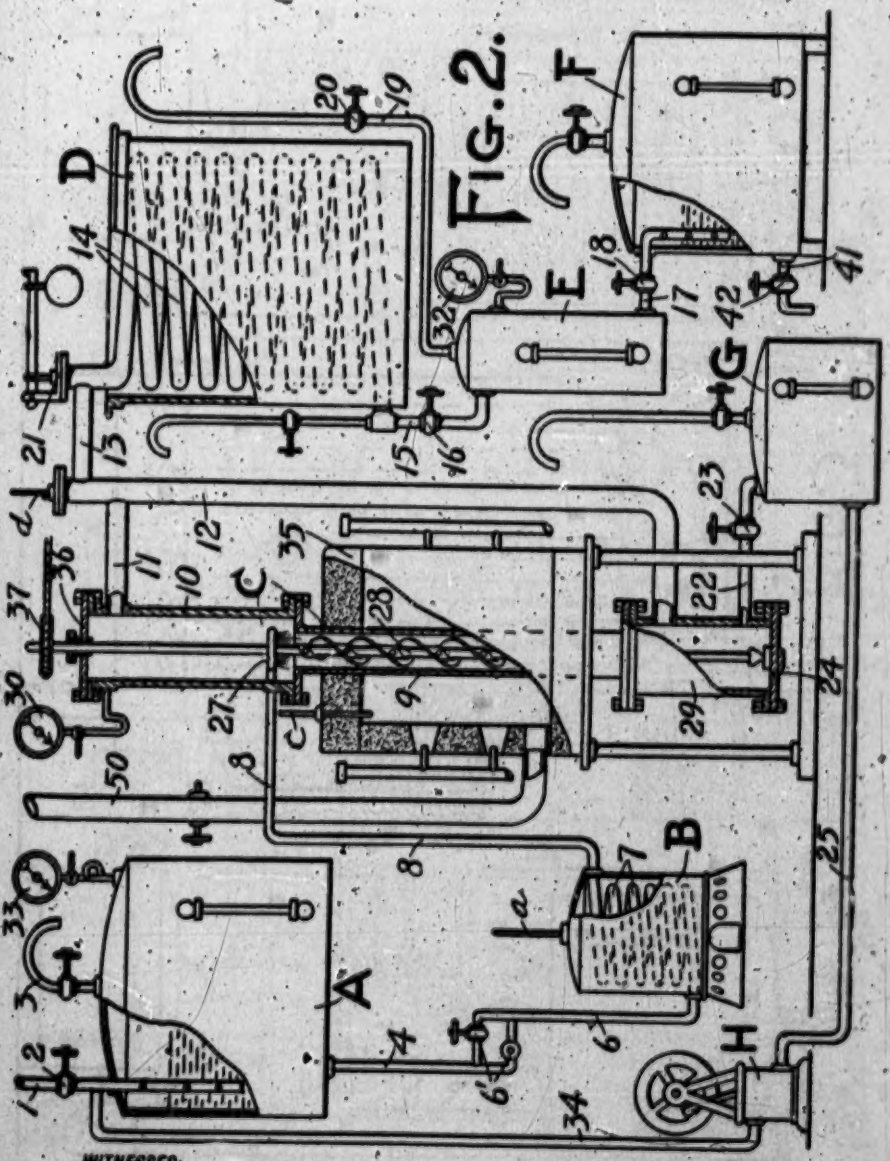
OIL CONVERTING PROCESS FOR THE CONVERSION AND TRANSFORMATION OF OILS

Filed June 15 1916 5 Sheets-Sheet 2



WITNESSES:

A. Capstick

J. Orl. Barbelang

INVENTOR

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4778

[fol. 1335]

July 24, 1923. 1,462,677

J. H. ADAMS

OIL CONVERTING PROCESS FOR THE CONVERSION AND TRANSFORMATION OF OILS

Filed June 15, 1916 5 Sheets-Sheet 3

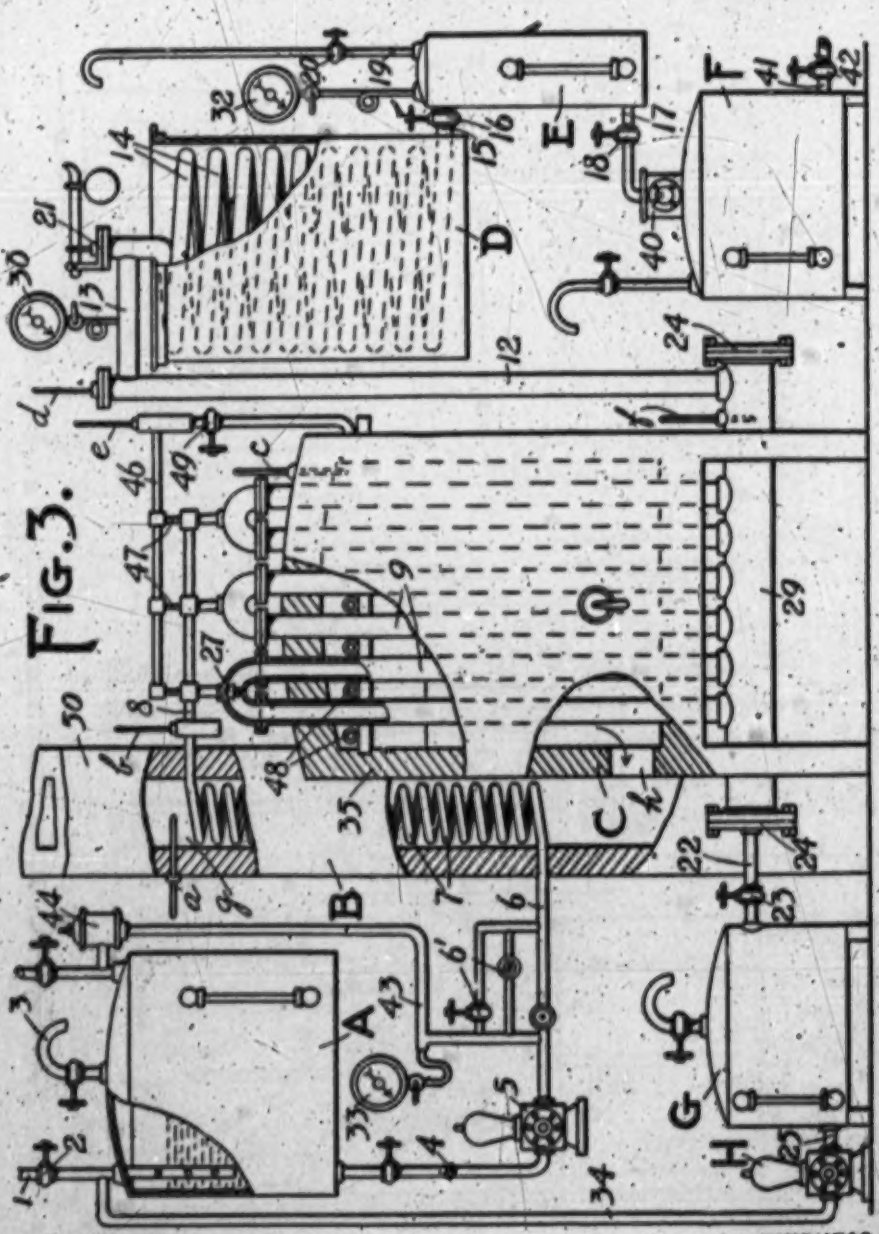

FIG. 3.

WITNESSES:

A. Capetuck

Joel B. Selzing

INVENTOR.

Joseph H. Adams

[fol. 1336]

July 24, 1923. 1,462,677

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OIL CONVERTING PROCESS FOR THE CONVERSION AND TRANSFORMATION OF OILS

Filed June 15, 1916 5 Sheets-Sheet 4

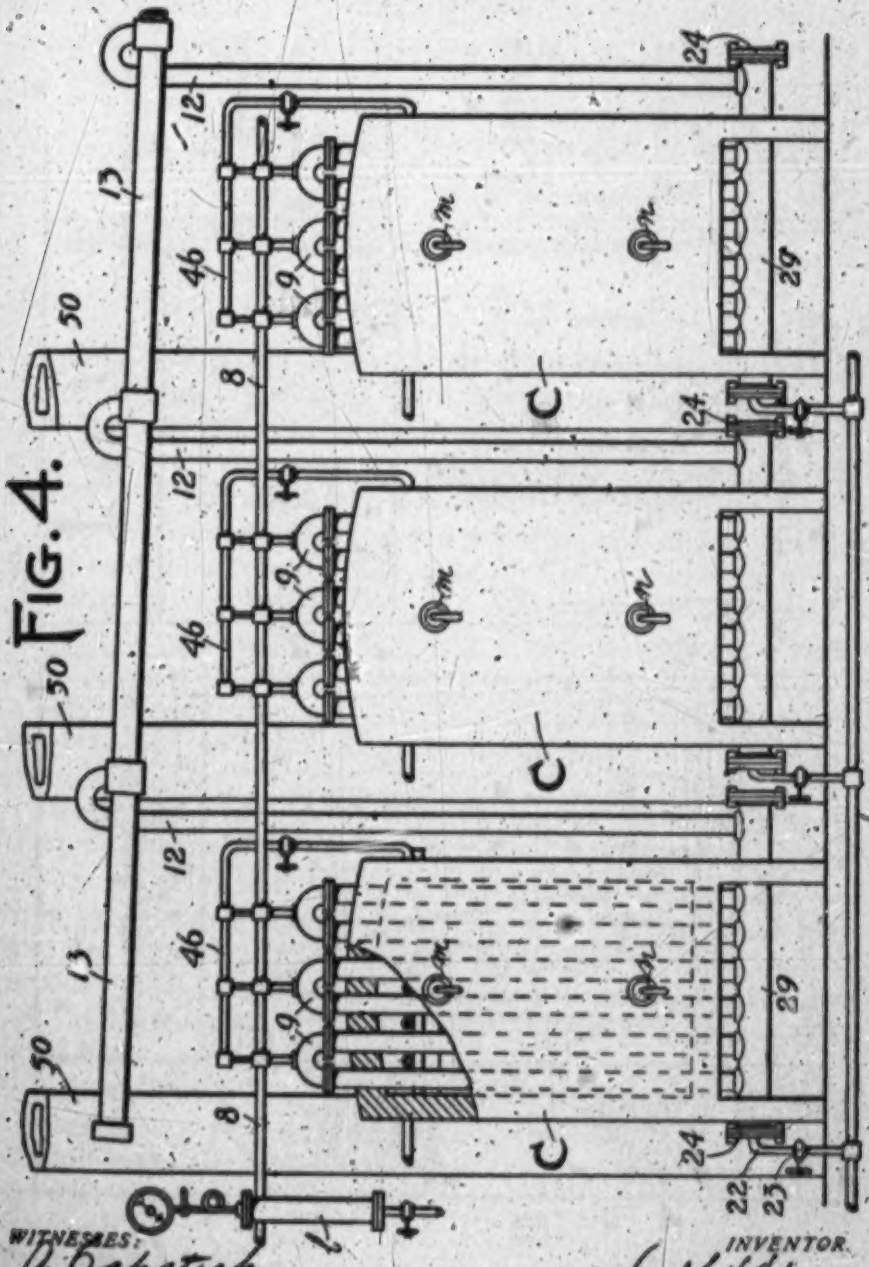


FIG. 4.

WITNESSES:

A. Capstick

Jos. B. Belding.

INVENTOR.

Joseph H. Adams

4780

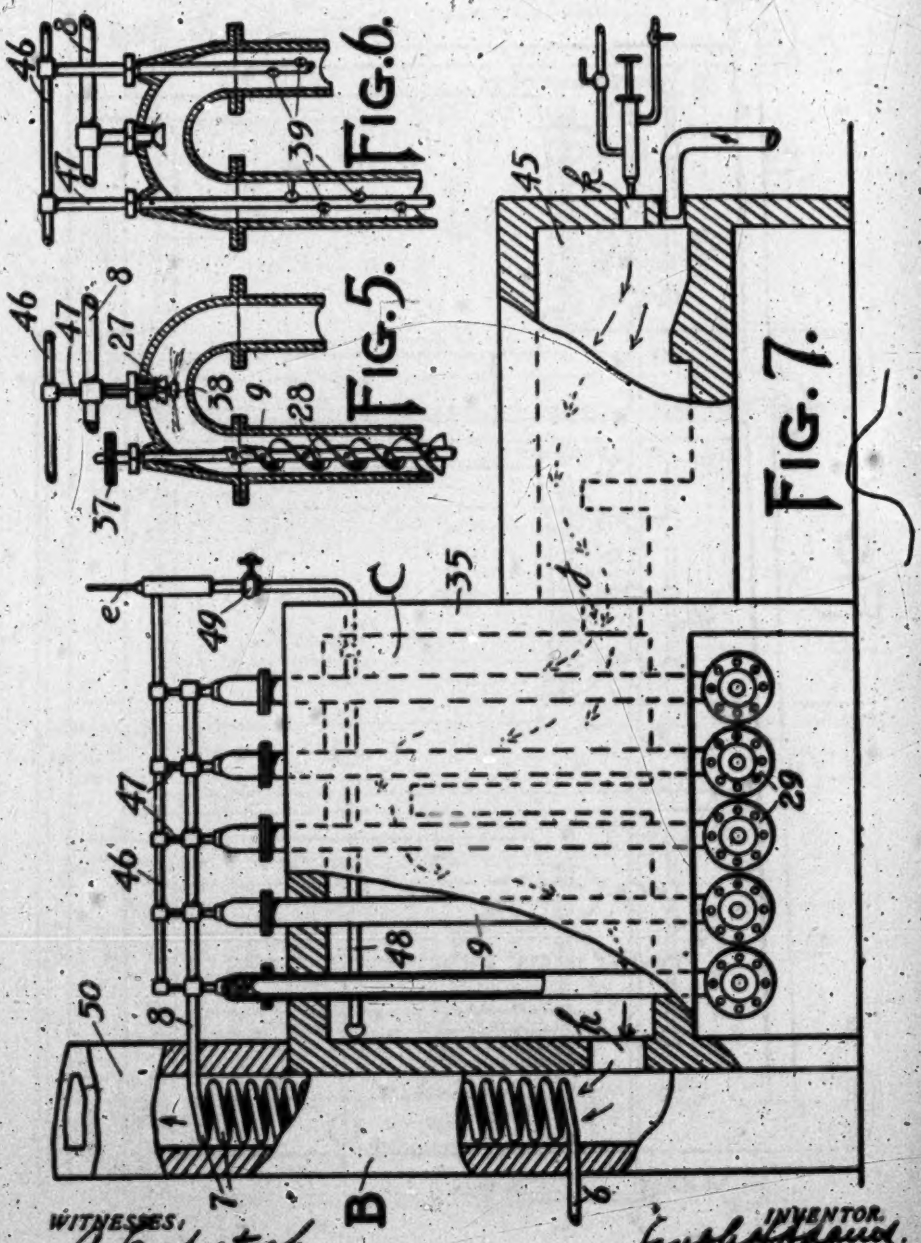
[fol. 1337]

July 24, 1923. 1,462,677

J. H. ADAMS

OIL CONVERTING PROCESS FOR THE CONVERSION AND TRANSFORMATION OF OILS

Filed June 15, 1916 5 Sheets-Sheet 5



[fol. 1338] Patented July 24, 1923. 1,462,677

United States Patent Office

Joseph H. Adams, of Flatbush, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Oil-Converting Process for the Conversion and Transformation of Oils

Application filed June 15, 1916. Serial No. 103,725

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Flatbush, in the county of Kings, and State of New York, have invented a new and useful Oil-Converting Process for the Conversion and Transformation of Oils, and of which the following is a specification.

This invention relates broadly to the art of converting fluids such as oils into products of dissimilar character from the original untreated oils, by heating the oils, vaporizing them under pressure, then cracking and transforming such oily vapors while under vapor pressure into lighter vapors which, as converted and when condensed under pressure, will result in lower boiling products from original high boiling oils.

In its more intense aspect the invention consists in a thermal and vapor pressure method of converting the vapors of semi and more or less refined mineral oils as those of the kerosene, non-viscous, neutral, gas, fuel and coal tar oils into more volatile and lower boiling hydrocarbons such as gasolenes, naphthas, benzines, benzol, tuluol and other light oils and oily spirits of both the aliphatic and aromatic series.

The apparatus illustrated and to be described as adapted for use in carrying out my process was invented by me but is not herein claimed since it is made the subject matter of another application Serial No. 103,726 filed of even date herewith.

One object of the invention is to formulate a process of a commercial nature for transforming higher boiling oils into lower boiling products by vaporizing the oil, cracking and

condensing the vapors while maintaining the whole system under pressure of the generated vapors.

Another object of my invention is to provide a simple and commercial process of cracking or converting high boiling hydrocarbon oil in the vapor phase into lower boiling products, and particularly to insure an efficient and effective conversion process by preliminarily heating the oil to substantially its boiling or vaporization point under superatmospheric pressure and then discharging or expanding it into vaporous form and cracking it in the vapor phase under superatmospheric pressure and cracking temperature, after which the evolved vapors are condensed and collected.

The invention is clearly distinguished from methods of fractional distillation by which hydrocarbon oils are commonly separated into distillates according to the respective boiling points thereof, inasmuch as by the practice of my invention the molecular construction of the higher boiling hydrocarbons is transformed so as to produce lower boiling point products.

It has been my purpose to effect this conversion in the least expensive and most practical manner and to that end my process and method embodies broadly some or all of the steps of first heating, then vaporizing the oil, then cracking and transforming the vapors at elevated temperatures while the oils and oily vapors are maintained under superatmospheric vapor pressures, and condensing the vapors under like pressures, the condenser being preferably in free communication with the converter.

In carrying out my invention in its preferred form, the oil is preheated to approximately its boiling or vaporization point under sufficient superatmospheric pressure to maintain it in liquid form. The highly preheated liquid oil to which the latent heat of vaporization has been supplied, in a state of incipient vaporization, is then discharged or released into an enclosed cracking chamber, which is maintained at a cracking temperature and at a superatmospheric pressure somewhat less than that under which the oil is preheated, whereupon the liberated oil expands and breaks into vaporous form in which it is subjected to the full cracking heat of the chamber and effectively cracked or converted in the vapor phase. The cracked vapors pass to

a condenser which is maintained at substantially the same pressure as that of the converter, the desired pressure being maintained by controlling the discharge of liquid and gases from the apparatus. By properly controlling the oil supply and the discharge of the generated products the process may be operated continuously.

Other objects and features of the invention will become [fol. 1339] apparent to those skilled in the art from the following description of a preferred illustrated embodiment of the invention.

In some cases oils of one series may be transformed into those of an entirely and essentially different series as the aliphatic into the aromatic or the chain into the ring series.

For example, a kerosene or gas oil distillate yielding no gasolene or naphtha by fraction distillation may, by this vaporization—heat—pressure method, be transformed into gasolene and naphtha, the heavy coal tar oils into benzol, tuluol and other lighter oils, while under different conditions, that is higher heats and pressures, petroleum oils may be transformed into aromatic compounds as benzene, benzol, toluol and other light oils.

The description of the process is facilitated by means of drawings showing apparatus adapted for carrying out the invention.

Referring to the drawings:

Fig. 1, is an elevation and partly sectional drawing of a simple apparatus adapted for carrying out my process.

Fig. 2 is an elevation and partly sectional drawing of another and more complete apparatus embodying additional details.

Fig. 3, is a partly sectional elevation drawing of a commercial type of apparatus more complete in detail and structure.

Fig. 4, is an elevation drawing of a battery of vapor converters showing the free communication of the units one with another.

Fig. 5, is a sectional drawing showing the manner of admitting super-heated steam to the oily vapors undergoing transformation.

Fig. 6, illustrates another method of introducing superheated steam to the oily vapors while being subjected to the powerful influence of cracking heats and high vapor pressures, and;

Fig. 7, is an elevation and partly sectional view of the heat exchanger for preheating ingoing oil, the combustion chamber of regenerative furnace and group of vertical vapor converting chambers enclosed within the body of the high temperature furnace.

In Fig. 1, of the drawing a simple form of apparatus is shown embodying the main elements of my invention and in Fig. 2, I have shown an apparatus adapted for carrying out the herein described process and having additional features not shown in Figure 1, while in Figures 3, 4, and 7 I have shown an apparatus of commercial capacity for carrying out my invention on a large scale, Figures 5 and 6 showing details of Figures 3, 4, and 7.

In these figures I have designated the main elements of the apparatus with letters of the alphabet whereas the specific parts are marked with reference numerals, the same reference characters being used to indicate corresponding parts in the three figures.

Referring particularly to the simple form of apparatus shown in Fig. 1, the reference character A, represents an oil supply tank from which the oil is supplied to the apparatus for the conversion process.

The oil passes from this tank A, through pipe 4, precision feed valves 6′ and pipe 6, to pre-heater B, in the coils or pipes 7 of which the oil is heated, then through pipe 8, to the tubes 9 and chamber 10 of converter C, where the hot oil breaks into spray or mist like vapor so that in such gaseous form it may come in contact with cracking heats within the tube coil 9 and chamber 10.

The pre-heater B, is of any preferred construction as a feed water heater, a small boiler or other form of heater, whereby the oil may be heated by suitable means in order to raise it in temperature substantially to, or approaching, the boiling or vaporizing point under the particular pressure employed, so that when admitted or sprayed into the cracking chamber or tubes it will break into vaporous form.

The converter C, embodies an outer casing 35, of heat enduring and insulating material for confining the heat and any suitable means may be provided for heating this chamber, such as oil or gas burners or other economical means of fuel consumption. I prefer making the converter itself in tubular form so that there will be a large

heating surface presented as compared to the volume of vapor undergoing conversion passing through the converter; and in the form shown in Fig. 1, the converter C comprises a pipe coil 9 and an enlarged chamber 10. The oil preheated under pressure to substantially its vaporization point, at that pressure in the preheater B, is delivered through valve 26 in a thin stream into the bottom of the coil 9 through which it rises and is then admitted into the enlarged chamber 10. Both the coil 9 and the chamber 10 are heated to intense cracking temperatures which are in excess of the temperature of the preheater. Therefore, as the oil, in a state of incipient vaporization, rises through the pipe 9 and into the enlarged chamber 10, the relation of heat to pressure is such that the oil in transit will break into and maintain a vaporous form in which it is cracked.

The vapors, after being subjected to the high temperature in the coils 9 and the enlarged chamber 10, pass out through pipe 11, to separating chamber 12, the lighter converted vapors rise and flow through pipe 13, to condenser D, where, in the coils 14, the vapors are passed [fol. 1340] down and condensed to liquid: and, together with the fixed gases generated during the process, are drawn off through pipe 15 and valve 16, into running trap tank E, which is provided with a draw off pipe 17, controlled by valve 18.

It will be understood that the supply tank A, can be refilled from time to time through the inlet pipe 1, and that the supply of oil from that tank to the converter C, may be augmented by air pressure which is applied over the surface of oil in the tank in order to force it into the preheater B, and so on into the converter C, the valve 2, being closed as well as the valve in vent pipe 3, and the air pressure being registered on pressure gauge 33.

The compressed air may be supplied from any suitable source (not shown) and may conveniently be introduced through the pipe 3 if desired. Sufficient pressure is thus maintained upon the supply of oil to force it through the preheater against the back pressure of the converter and to hold the heated oil in liquid form while being raised to substantially its corresponding boiling point and until it is

introduced by releasing or spraying it into the converter in which it immediately vaporizes and is cracked.

The pre-heater B, is intended only to heat the oil sufficiently to cause its easy vaporization when admitted to the converting chamber or coils 9, through pipe 6, and is not intended to perform any cracking operation; the heated oils at the time of admission to the said chamber then being at a temperature sufficient to immediately vaporize and expand them for the vapor conversion process.

The temperature of the converter C, is raised to such a point as will crack or convert the oily vapors into lower boiling products or convert them into products having essentially different natures.

By reason of the preheating of the oil to substantially its vaporization point, the heat of the converter is fully expended in effectively cracking the oil in the vapor phase.

It will be seen that the condenser D, is in open communication with the converter C, through pipe 11, and separator 12, and therefore any pressure in the converter will extend to and through the condenser.

The continual feeding of new quantities of hot oil to the apparatus will build up or raise the vapor pressures in the converter; and consequently throughout the condenser, so that the vapors undergoing the cracking operation will at all times be under superatmospheric pressures while being subjected to cracking heats. This pressure is of course the result of the expansion due to the vaporization and heat and is somewhat less than that utilized to force the oil through the preheater and hold it in liquid form.

This pressure maintained in the converter and through the condenser may be regulated by controlling the discharge of the fixed gases which are always generated to a more or less extent in the converter.

The condensation of vapors also tends to reduce the pressure and thus control of the escape of fixed gases is sufficient to enable the operator to maintain the pressure desired.

The fixed gases pass out with the condensed vapors through the pipe 15, into the trap tank E, and their escape through the pipe 19, is controlled by valve 20.

When the process is in operation pressure in the converting system will be registered on gauges 30 and 32,

which, under normal operative conditions, should both indicate the same uniform pressure, while for safety purposes in this high pressure system, comprising pre-heater B, converter C, condenser D, and the running trap tank E, the release blow off valve 21, is provided and located about over the condenser D.

The gauges 30 and 32, register vapor pressures while in this form of apparatus gauge 31, on the pre-heater B, registers the oil pressure which in all cases should be below the pressure maintained over the oil in supply tank A, as registered on gauge 33.

Vapors which pass out from the expansion chamber 10, through pipe 11, and into the separator column 12 may there be separated into the lighter ones, which pass to the condenser D, and heavier partially or wholly unconverted vapors which will drop to the bottom of the column together with particles of coke or carbon.

The bottom of this chamber 12, is connected to overflow hot oil tank G, by means of pipe 22, the flow of oil through which is regulated and governed by valve 23, and this column 12, is also provided with a detachable plate 24, so that solid or semi-solid matter and deposit may be removed from time to time. The material collecting in the tank G may be returned to the supply tank for further treatment, the pump H serving to draw off the oil through the line 25 and return it to the tank A through the line 34.

The drawing Fig. 2, presents a partly sectional elevation of an apparatus adapted to carry out my process embodying a suitable oil supply tank A, and air pressnre pump H, to maintain pressure over the surface of oil in the tank in order to force it into converter C, through pre-heater B, against a high back or vapor pressure while maintaining it in liquid form; a converter C, in tubular form enclosed within a high temperature furnace 35, a condenser D, and liquid running trap E, in free communication with the converter, [fol. 1341] an enclosed running tank F, for the distillates of converted oils connected with the trap E and tank G, for partly or wholly unconverted oils which may be removed from time to time from the lower or heavy bottoms chamber 29, and returned through pipe 25 and pump H, to supply tank A, for retreatment. These parts correspond in operation to similar parts shown in Fig. 1.

The drawing Fig. 2, shows one of the many forms of tubular converters which may be employed in my process..

At the upper end of the tube 9, an expansion chamber 10, permits the lighter converted vapors to become more or less separated from the heavier ones and pass out through the vapor pipe 11, to condenser D, while the heavier partially or wholly unconverted vapors drop back and down through the tube 9, for further treatment, while the very heavy ends as well as any carbon cracked out in mineral form may precipitate or fall into the heavy bottoms chamber 29, located below the tube.

This chamber 29, is connected to overflow oil tank G, by means of pipe 22, regulated by valve 23, and is provided with a detachable plate 24, so that solid matter may be removed at times as required.

The heated oil is delivered by spraying it in at the upper end of cracking tube 9, through a perforated collar or circular nozzle 27, which, with its own heat and the intense temperature of the converter, drives the oil into a vapor or mist like condition ready for contact with the cracking heats while held under superatmospheric pressures during the process.

As the oily vapors pass down through the tube 9, a part or all of them are converted into lower boiling products and while some of them flow out through pipe 11, leading from the upper expansion chamber 10, others flow through pipe 12, leading from the lower or heavy bottoms chamber 29 and through the condenser D. This pipe connection furnishes free and open communication between the converter C and the condenser D and permits an equalization of pressure.

As an added feature of importance in this vertical type of tubular converter a rotor 28, provided with a helical strip of metal attached in screw like position on the shaft can be employed to remove the accumulation of carbon in the tubular chamber 9.

The shaft, which extends through the cap 36, and is provided with a stuffing box and which has a bearing at the lower end in the detachable plate 24, of the heavy bottoms chamber 29, can be revolved by power applied to a sprocket wheel 37, located a short distance above the cap 36, and

driven by chain gear so that it will revolve and remove the carbon.

Any free carbon held in suspension in the cracked vapors or precipitated therefrom will drop into the heavy bottoms chamber 29, through tube 9, or pipe 12, so that vapors led into condenser D, may be in part or wholly freed from mineral carbon; and any carbon adhering to the inside of the vertical tube may, by means of the revolving rotor 28, be nipped off and caused to drop into the chamber 29, below the tube.

Referring now to the drawing Fig. 3, the source of supply or oil tank A, may be located at any required distance from the preheater B, and by means of pump 5, the oil is delivered continuously into the tubes 9, of converter C, through the heating coils 7 and pipe 8, to replace that which is continually withdrawn from the converter in the form of vapors.

Pump 5, is provided to draw oil through pipe 4, and force it through precision valves 6, pipe 6, pre-heater coils 7 and pipe 8, into the tops of converting tubes 9, of converter C.

It is always best to pre-heat original oil before admitting it to the vaporizing system so that the heat from the furnace may be conserved for the purpose of cracking the vapors of oils and not for pre-heating it to a cracking temperature; and to this end the waste heat from the furnace as it escapes through flue *h*, into the throat *g*, of stack 50, can be economically applied in this form of exchanger to the purpose of heating original inflowing oil through pipe coils 7.

The oil so heated is forced into the tubes of converter C, through pipe 8, which delivers it to the several spray nozzles 27, at the heads of the tube connections against a back or generated vapor pressure maintained in the tubes 9, and throughout the several following parts of the system comprising the carbon and vapor chamber 29, the tubes 14 of condenser D, running trap tank E, and the intervening vapor and liquid pipes 12 and 13, 15 and 17, valve 16 and both sight glasses and pressure gauges located on the apparatus.

This drawing Fig. 3, shows one of the many forms of tubular converts which may be employed in my process, and in this type of apparatus a multiple of heat enduring

tubes 9, constructed of materials capable of withstanding intense temperatures and high pressures are located vertically in the high temperature furnace and enclosed within fire brick walls 35, designed to withstand protracted high temperatures and cracking heats. These chambers or tubes 9, are connected into a header or heavy bottoms chamber 29, at their lower ends and are assembled in groups attached to each header 29, so that the entire group composed of two or more headers may receive the greatest effi- [fol. 1342] ciency from the furnace heat which may be generated in a primary chamber and passed into this furnace of converter C, or the heat generated primarily in the furnace enclosure containing the tubes, as a matter of mechanical efficiency.

This feature of tube arrangement is clearly shown in Fig. 7, and while it is not claimed by me as new, it is shown to illustrate the manner of placing tubes 9, as closely together as possible in order to present the greatest area to heats and heat currents generated in the fire box 45, or the principal chamber of converter C, which arrangement facilitates the efficiency of the process.

At the lower outgoing ends of the series of tubular chambers 9, vapors are led into a carbon and oil vapor trap 29, where any free carbon accumulated during the process is swept by the current of oily vapors in the tubes. This trap 29, is provided with detachable plates 24, at its ends for cleaning out purposes and leading from one or both ends of the chamber a vapor pipe 12, conducts light converted vapors to coils 14, of condenser D.

Any free carbon which may be held in suspension in vapors issuing from the converting tubes 9, may have a chance to precipitate to the bottom of this header or trap 29, and from vapor line 12, while vapors are rising therein so that vapors led into the condenser — may be in part or wholly freed from mineral carbon.

Any oils or condensed vapors caught in the bottom of trap 29, may be intermittently or continuously withdrawn through pipe 22 and valve 23 into hot oil collecting tank G, from which they may be withdrawn through pipe 25, by pump H, and returned to oil supply tank A, through pipe 34.

The vapor line 12, rising from one end of the chamber 29, conducts vapor into the coils or pipe 14, condenser D,

which latter may assume any of the forms employed in the oil refining industry.

The coils or pipes 14, of condensing apparatus D, are ordinarily immersed in cold water and the rapidity of condensation as well as the quality of product can be partially controlled by the temperature of the water surrounding these condensing coils or pipes.

Condensate accumulated in the condenser runs without interruption into an enclosed collecting or running trap tank E, freely connected therewith by pipe 15 and valve 16, from which it is withdrawn into running tank F, through pipe 17 and valve 18, after passing sight box 40.

Any accumulation of distillate in the tank —, may be drawn off through pipe 41 and valve 42, to make room for newly and continuously admitted distillates from trap tank E.

The vapor pressure is indicated and regulated as in the form shown in Fig. 1.

In feeding oil to the system through pump 5, the pump cannot be so accurately regulated as to constantly deliver the required amount of oil into the converter chambers, therefore a return pipe 43 and enclosed pop or release valve 44, will permit any excess oil not delivered into the system to be returned to the supply tank A.

This pop valve 44, can be set at any tension ten or fifteen pounds or more greater than the pre-determined number of pounds pressure maintained in the system and with the pump 5, operating under normal conditions all oil not delivered through the precision valves 6′, will be returned under pressure to the tank A, through the release valve 44, and such pressures may be constantly known and under observation by means of gauge 33, arranged in the excess oil line 43, so as to be constantly informed as to the conditions under which the pump 5, is working.

Thermometers and pyrometers *a*, *b*, *c*, *d*, *e* and *f*, are placed at several important locations on the apparatus so that a comprehensive idea may be had as to temperatures of heats, vapors, steam, etc.

A feature of primary importance in this invention is simplicity in the operation of the process in a suitable apparatus as well as the rapid, continuous and safe method of oil and oily vapor transformation to produce large yields of low boiling hydro-carbons and other oily products.

The multiplicity of tubular converters present large surfaces to the furnace heats in proportion to the amount of oil in vapor form contained in the tubes, and this the yield of light distillates will be rapid and the quality high in desired products.

A considerable number of tubes having a comparatively small diameter of from two to eight inches may be so arranged as to present from four to six times greater surfaces to the intense furnace heat than the parts of tubes extending through and beyond the furnace walls for terminal and return fittings, if such an arrangement is employed.

When the supply pump 5, is in operation oil will be constantly flowing under pressure through the coils 7, of preheater B, into the cracking chambers, being admitted through spray nozzles 27. The spray or vapors takes the place of that already converted and condensed.

This newly admitted oily spray or vapor will in turn be superheated, cracked and sub-divided into finer vapors and changed in the apparatus into lighter or more volatile products by splitting the molecules of or rearranging them and breaking out a small portion of carbon.

In this manner the complex mixture of oils known commercially as kerosene, gas, fuel, coal tar, creosote, and [fol. 1343] others may be changed by means of my process into mixtures of lighter oils which bear a general resemblance to those which are commercially known as naphtha, gasolene, benzine, benzol, toluol, and other light oils and oily spirits.

It may here be mentioned that during the operation of the process the raw non-converted oils will be relieved of a percentage or portion of mineral carbon which, due to the intense cracking heats, may assume the form of fine particles of coke and in this method of oil transformation the chemical character of the vapors may possibly be changed from one or more of the products of the hydrocarbon series into others of an essentially different character and series.

The carbon which is removed in this manner will be in part deposited in the tubular converters and in part precipitated in the carbon and vapor trap 29, as the certain small portion broken out in the process may be held in suspension in the vapors during a part of their course through

the converting tubes 9, and adjacent pipes and condensing tubes 14, of apparatus D.

The continual circulation of oily vapors through the tubes permits the intense heat to act rapidly and convert high percentages of the subjected vapors into desired products and the small quantity of vapors contained within such tubes, traps, cooling coils and vapor lines assures a certain degree of safety in the operation of this apparatus for if a break should occur in any part of the converting system under pressure, the fire which might result would be confined principally to a very few barrels or gallons of oil in vapor form undergoing treatment rather than a still full of liquid material.

The furnace of converter C, may be operated in any convenient manner with coal, fuel oil, gas, electricity or other economical and easily obtainable heat producing medium, but for uniformity of result, economy and generally satisfactory operation, a fuel oil burning equipment is at the present time and for general localities, the most practical method of generating intense temperatures such as are required in the furnace of this converter.

Almost any of the efficient oil burning systems are adapted to this work but as that part of the apparatus is not a feature of this process any specific description is avoided beyond the indication of a burner projecting into the opening *k*, of the combustion chamber 45, of Fig. 7, the flues *j* and *h*, and in the location of the stack 50, rising from the side or rear of the converter C, for draught or vent purposes.

As a feature of safety in this high temperature and pressure process the release blow off valve 21, is preferably located at a distance away from the converter, usually at the end of the vapor line 13, just above the condenser D.

In commercial practice where it is desirable to convert oil on a large scale it will be necessary to employ a number of converters in the same plant and in that case they should be arranged in battery form and should be so connected that the vapor pressure from each will be transmitted to the others thus operating all under the same pressure.

Any tendency toward a drop in pressure in one converter will be compensated for by the pressure from the others and thus easier and more perfect regulation may be secured.

This arrangement is shown in Fig. 4, where a battery of converters C—C—C, are spaced apart the required distance for mechanical operation and the proper arrangement of connecting pipes and pipe connections, the hot oil being forced through pipe 8, and delivered to the tubular converting chambers 9, in each of the converters.

The converted and transformed vapors pass out through traps 29, into the vapor line 12, leading to the condenser where they are reduced to distillates in the tubes 14.

As each one of the tubular converting units comprising the chambers 9, are freely connected with the vapor line 13, by means of the pipes 12, leading out from the top of traps 29, and this vapor line leads freely to and is in open communication with the condenser in which vapors are condensed under vapor pressures maintained throughout the converting system, it will be seen that two or more converts comprising a battery will be equalized in operative vapor pressure through the vapor line 13, or other vapor lines which may be employed to connect and compensate the several converters for the purpose of equalizing and maintaining uniform pressures in the vapors undergoing transformation in such a battery of converters.

This unit battery feature and the freely connected converters one with another, in its broadest aspect was first adopted by me and employed as described in my co-pending application Serial No. 530,852, filed Dec. 1, 1909, which matured on October 28, 1919, into Patent 1,320,354, and is claimed in Patent 1,433,519, which is a division of said patent and was granted on October 24, 1922.

As an added feature of importance in this method of oily vapor transformation I may also use super-heated steam injected while at elevated temperatures into the body of oily vapors through one or more of the tubular converters 9, as indicated by the pipe 46, and jets 47, shown in Fig. 3, and on a larger scale in Figs. 5 and 6, the steam being generated outside the apparatus but may be super-heated [fol. 1344] to any degree in the super-heating coils 48, of Fig. 3, and Fig. 7, by the heats generated within the furnace of converter C, to which coils it may be admitted from outside and controlled in its entry into the oily vapors by valve 49.

The pipes 47, employed for such admission of steam may be more clearly seen in the drawing Fig. 5, where

one is shown projected into the top of an oil inlet and return bend connecting two tubes, the steam flowing through pipe 46, and admitted to the interior of the converters by pipe 47 and a small perforated jet 38, at the bottom of the pipe through which the super-heated and gaseous steam is forced under higher pressure than that maintained in the converting system.

As a matter of convenience and mechanical practicability, I may also introduce the steam into tubes 9, by projecting the steam pipe or pipes 47, into the end of one or more tubes, as shown in Fig. 6, carrying it down a part of or all of the length of each tube and providing the pipe with suitable openings or jets 39, for the proper admission of steam, which same is controlled by valve 49.

I ordinarily super-heat the steam above 800 to 1000° F. and when admitted and mixed with oil and oily vapors it possesses advantages both in hydrogenating oils and reducing mineral carbon deposit while at the same time the resultant distillates are superior in odor and color, and I therefore intend that this feature may be employed in this process as a matter of practical and mechanical convenience at such times as the operator may find it advisable to introduce the same for the purposes described.

I may also employ rotors 28, in these vertical tubes as shown at the left side of Fig. 5, and install them as shown in Fig. 2, for the principal object of removing carbon from the interior of the tubes 9.

Having filled the reservoir tank or source of supply A, with original oil to be converted the fires are started in the furnace of converter C. Oil is admitted into the converting chamber 9, in small sprayed or vaporized quantities continuously, and as it falls through the chambers, becomes super-heated and is withdrawn through pipe 12, into the condenser D, and any heavier un-converted liquid portions which fall into the chamber 29, are drawn off from time to time or continuously and returned by pump H, to the supply tank A, until the coil 7, in the pre-heater B, has been raised in temperatures sufficient to bring the oil to its bo-ing point under the pressure maintained in the pre-heater, and the tubes are heated to vapor cracking temperatures which may be determined by the pyrometer installed in the system, and the vapor pressure in the converter and condenser begins to rise.

The temperatures should finally be sufficiently elevated to prevent condensation of vapors while contained in the tubes and as soon as the tubes 9, are full of vapors and the temperature increased until it reaches the required cracking heat it is then maintained at that temperature which will render the best conversion results continuously while the vapors are held under vapor pressures.

In this operation some of the vapors will necessarily be changed to fixed gases and some of the vapors will not be converted but a large proportion will be converted into lower boiling products essentially different in nature from the original material.

When the products pass from the converting tubes 9, into the trap 29, some of the unconverted oils of high boiling point will condense and may be drawn off through pipe 22 and valve 23, while the converted vapors and fixed gases will rise through pipe 12, and pass into the coils 14, of the condenser D. The converted vapors are here condensed and pass with the fixed gases into the trap tank E, from which they are drawn off in liquid form into tank F, through pipe 17 and valve 18.

The fixed gases are carried off by pipe 19, and the valve 20, in that pipe may be so adjusted as to allow the escape of so much gas as will maintain the desired pressure in the converter and condenser.

Preferably the process is operated as a continuous one, oil being continuously supplied from tank A, through pre-heater B, to the converted C. The operation of forcing or spreading the hot oil into the converter where it immediately vaporizes and the generated self-imposed pressure of the vapors due to the cracking operation tend, of course, to raise the pressure in the converter but this is compensated for by the condensation of the vapors in the condenser and the regulated escape of fixed gases and thus, even in the continuous operation, the pressure may be maintained at the number of pounds desired throughout the continuous use of the process.

It will be understood by those skilled in the art that the temperature necessary in the pre-heater B, converter C, and the pressure of the vapors in the converter through the condenser will vary with the characteristics of the particular oil being treated and therefore it is not possible to state any definite figures which would be applicable to all

oils. The operator may determine when he gets the proper temperature in the converter by the character of the product coming from the condenser. As illustrating the adaptability of my process for use with oils of widely different boiling points and of widely different characters it may be said that a kerosene distillate with an initial boiling point [fol. 1345] of 300° F. can be converted into distillate having an initial boiling point below 100° F. and a heavy paraffine gas oil having an initial boiling point of 400 to 500° F. can be converted into a distillate having a boiling point of 100° F. or less.

If, in the use of my process, it is desired to secure the greatest yield of gasolene the operation should be so regulated as to obtain a converted product having an initial boiling point of 100° F. or less.

Subject to variations, in accordance with the particular oils and operating conditions, I now believe that the present process of oil conversion is preferably conducted at temperatures from 1000° to 1200° F. and at pressures of from 70 to 90 pounds in the cracking converter. The temperatures might in some cases run as low as, or even lower than 900° F. or as high as 1500° F., while the operating pressures might range between 50 and 100 pounds or even considerably higher. The process, however, is primarily a vapor phase process and, therefore, the operating temperatures preferably will be somewhat higher than those commonly employed in processes of oil conversion in the liquid phase.

While it is possible to bring about these changes and convert higher into lower boiling compounds it is impossible to broadly state specific pressures and temperatures applicable to oils in general as the natures of crude hydrocarbons as well as the distillates of crude oils vary so greatly in their composition and qualities that it is impossible to apply a fixed rule to oils in general and particularly to those which as a matter of commercial advantage would be available for conversion by the application to them of this process.

The present invention relating to the process is, of course, not limited to the use of a specific apparatus and it may be performed in various ways. I believe the fundamental steps of the process above set forth to be broadly new and

by the language employed in the following claims it is my intention to cover that process in its broadest aspect.

Having described my invention what I claim as new and desire to secure by Letters Patent is:

1. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater under superatmospheric pressure to substantially its corresponding boiling point, delivering the heated oil into a chamber where it breaks into vaporous form, maintaining substantially the same superatmospheric pressure on the oil vapors in the chamber and subjecting the oil vapors therein to a cracking temperature whereby the oil is converted in the vapor phase.

2. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater to substantially its boiling point under sufficient superatmospheric pressure to maintain it in liquid form, releasing the heated liquid oil into an enclosed chamber where it breaks into vaporous form, maintaining on the vapors in the chamber substantially the same superatmospheric pressure and subjecting the vapors in the chamber to cracking temperature to effect a conversion thereof in the vapor phase.

3. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising continuously supplying oil under superatmospheric pressure in a confined stream, heating the oil in a preheater as it passes to substantially its boiling point corresponding to the pressure employed while still maintaining it in liquid form, discharging the heated liquid oil into an enclosed chamber where it breaks into vaporous form, and maintaining the oil vapors under substantially the same superatmospheric pressure and at a cracking temperature whereby they are converted in the vapor phase.

4. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preliminarily heating the oil in a preheater to a point of incipient vaporization, discharging it in vaporous form into a chamber, heating the vapors therein to a cracking temperature, conveying the evolved vapors through a con-

denser in open communication with the chamber and so regulating the discharge of the resultant product as to maintain a substantially uniform superatmospheric pressure in the condenser and the chamber.

5. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater under superatmospheric pressure to substantially its corresponding boiling point while maintaining the oil in liquid form, admitting the preheated liquid into a chamber under superatmospheric pressure somewhat less than the pressure under which the oil is preliminarily heated, where it breaks into vaporous form, and subjecting the vapors in the chamber to a cracking temperature to convert them in the vapor phase.

6. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater under superatmospheric pressure to substantially its boiling point at that pressure, delivering the heated oil in vaporous form into a confined chamber, subjecting the oil vapors therein to superatmospheric pressure and to a cracking temperature whereby [fol. 1346] the oil is converted in the vapor phase and condensing the converted vapors under superatmospheric pressure.

7. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater under superatmospheric pressure to substantially its boiling point at that pressure while maintaining it in liquid form, delivering the heated oil in vaporous form into an enclosed chamber against a back pressure, subjecting the oil vapors therein to a slightly reduced superatmospheric pressure, heating the oil vapors while under said pressure to a temperature sufficient to effect their conversion and condensing the resultant product under superatmospheric pressure.

8. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising continuously heating the oil in a preheater under superatmospheric pressure to substantially its boiling point while maintaining it in liquid form, continuously delivering the heated oil into an enclosed chamber and against a back

pressure where the oil breaks into vaporous form, subjecting the oil vapors therein to a slightly reduced superatmospheric pressure, heating the compressed vapors to a cracking temperature and condensing the converted vapors under superatmospheric pressure and in open communication with the compressed vapors undergoing conversion whereby the oil is converted and condensed at a substantially uniform superatmospheric pressure.

9. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising heating the oil in a preheater under superatmospheric pressure to substantially its boiling point, delivering the heated oil in vaporous form within an enclosed chamber, maintaining the oil vapors therein under substantially the same superatmospheric vapor pressure, subjecting the vapors under pressure to a cracking temperature to convert the oil in the vapor phase, condensing the converted products under said superatmospheric vapor pressure and collecting the resultant low boiling condensate.

10. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preliminarily heating the oil in a preheater under superatmospheric pressure to a point of incipient vaporization, delivering the oil in vaporous form into an enclosed chamber and against a back pressure, maintaining the oil vapors in the chamber under a slightly reduced self-imposed superatmospheric vapor pressure subjecting the oil vapors while under pressure to a cracking temperature, causing the oil in vaporous form to flow continuously through the chamber while subjected to heat and pressure whereby the vapors are cracked and converted, and withdrawing the converted vapors and condensing them under superatmospheric pressure while continuously supplying additional oil in vaporous form to compensate for the withdrawal of the converted vapors.

11. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preliminarily heating the oil under pressure in a preheater to substantially its boiling point and delivering it in vaporous form into an enclosed chamber and against back vapor pressure, subjecting the oil vapors in the chamber to

sufficient superatmospheric vapor pressure and temperature to effect their conversion, condensing the converted vapors under said superatmospheric vapor pressure and returning the partially or wholly unconverted oil to the chamber for retreatment.

12. A process of converting high-boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preheating the oil in a preheater under superatmospheric pressure to substantially its corresponding boiling point while maintaining it in liquid form, delivering it to an enclosed chamber subjected to substantially the same superatmospheric pressure and to a cracking temperature whereby the oil breaks into vaporous form and is converted in the vapor phase, withdrawing and condensing the converted products as they are evolved and removing from the cracking zone the carbon produced during the cracking operation.

13. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preheating the oil in a preheater under superatmospheric pressure to substantially its corresponding boiling point while maintaining it in liquid form, spraying the heated liquid oil in vaporous form into the top of an enclosed chamber and subjecting the oil vapors in the chamber to a cracking temperature and to substantially the same superatmospheric pressure whereby the vapors are cracked and converted.

14. A process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase comprising preheating the oil under superatmospheric pressure to substantially its corresponding boiling point while maintaining it in liquid form, delivering the heated oil in vaporous form into the top of an enclosed chamber, delivering steam into the chamber concurrently with the heated oil and heating the mixed vapors and steam in the chamber to a cracking temperature while maintaining them under superatmospheric pressure whereby the oil is cracked and converted in the vapor phase.

15. A process of converting hydrocarbon oil into lower [fol. 1347] boiling products in the vapor phase, comprising preheating a continuously moving stream of oil under superatmospheric pressure to a point of incipient vaporization, continuously spraying said heated oil, together with superheated steam, into an enclosed chamber in mist-like vaporous form, heating the vapors in said chamber to a cracking temperature while maintaining a superatmospheric pressure insufficient to hold them in liquid form at the temperature employed, and drawing off and condensing the cracked vapors.

16. A continuous process of converting high boiling hydrocarbon oil into lower boiling products in the vapor phase, that comprises heating a continuously moving stream of oil under superatmospheric pressure to substantially its corresponding boiling point while maintaining it in liquid form, continuously spraying said heated oil in vaporous form, together with superheated steam, downwardly into an enclosed chamber, heating the vapors in the chamber to a cracking temperature while maintaining a superatmospheric pressure insufficient to condense the lighter vapors at the temperature employed, removing the residue material from the lower part of the chamber and withdrawing the lighter vapors from the upper part of the chamber and condensing them, while maintaining substantially the same pressure as in the chamber during the condensation.

17. A continuous process of converting high boiling hydrocarbon oil into lower boiling products, that comprises continuously heating a moving stream of oil under superatmospheric pressure to a point of incipient vaporization, spraying the heated oil into the top of said chamber where it breaks into vaporous form, spraying superheated steam into said chamber where it mixes with the vaporous oil, heating said chamber and its contained vapors below its upper end and above its lower end to a cracking temperature while maintaining a superatmospheric pressure on the vapors insufficient to condense the lighter vapors at the temperature employed, continuously removing the generated carbon and heavy residue downwardly out of the heating zone where it is collected, withdrawing the heavy residue, including the carbon, so collected below the heating

zone and withdrawing the cracked vapors evolved in the heating zone and condensing them under superatmospheric pressure.

18. A process for converting high boiling hydrocarbon oil into lower boiling products that comprises externally heating a plurality of vertical converter tubes to a cracking temperature, forcibly delivering oil from a supply tank to the upper ends of said converter tubes and passing the oil therethrough to be cracked in transit, collecting carbon and heavy residue at the lower ends of said converter tubes, separately removing the evolved vapors and unconverted liquid oil from the lower ends of said converter tubes, returning the unconverted liquid oil to the supply tank for retreatment and maintaining superatmospheric pressure upon the oil under treatment.

19. A process for converting high boiling hydrocarbon oil into lower boiling products that comprises externally heating a plurality of vertical converter tubes intermediate their ends to a cracking temperature, forcibly delivering oil to the upper ends of said converter tubes and passing it therethrough to be cracked in transit, collecting carbon and heavy residue at the lower ends of said converter tubes, removing the evolved vapors from the lower ends of said converter tubes and effecting their condensation, and maintaining superatmospheric vapor pressure upon the oil in process of conversion and condensation.

20. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises externally heating a plurality of vertical converter tubes intermediate their ends to cracking temperatures, forcibly delivering oil from a supply tank to the upper ends of the converter tubes and passing it in flowing streams therethrough to be cracked in transit, collecting carbon and heavy residue emerging from the lower ends of said converter tubes, removing evolved vapors from the lower ends of said converter tubes and effecting their condensation, separately withdrawing unconverted liquid oil from the lower ends of said converter tubes and returning it to the supply tank for retreatment, and maintaining superatmospheric vapor pressure on the oil under treatment throughout the system.

21. A process for converting high boiling hydrocarbon oil into lower boiling products that comprises externally heating a vertically disposed converter intermediate its ends to a cracking temperature, forcibly delivering oil to the upper end of said converter in sprayed or vapor form and passing it therethrough to be cracked in transit, preheating the delivered oil before its introduction into a converter, delivering superheated steam into the upper end of the converter in commingled relation with the sprayed oil, collecting carbon and heavy residue emerging from the lower end of said converter, removing the evolved vapors from the converter and effecting their condensation and maintaining superatmospheric pressure upon the oil during its preheating, conversion and condensation.

22. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing oil under pressure in flowing streams through a [fol. 1348] battery of converters independently, separately heating the respective converters of the battery to cracking temperatures, subjecting the oil in the several converters to superatmospheric pressure, equalizing the pressures in the several converters by maintaining free and open communication between the vapor spaces thereof, separately removing the evolved vapors from the respective converters and delivering them to a common vapor line and condensing the vapors received from the common vapor line.

23. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises continuously passing oil under pressure in flowing streams through a battery of converters independently, separately heating the respective converters of the battery to cracking temperatures, subjecting the oil in the several converters to superatmospheric pressure, equalizing the pressures in the several converters by maintaining free and open communication between the vapor spaces thereof and removing and condensing the vapors evolved in said converters.

24. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises separately charging oil in flowing streams through a battery of converters independently heated to cracking temperatures under superatmospheric pressure, equalizing the superat-

mospheric pressures in the several converters by maintaining their vapor spaces in free and open communication, separately removing the vapors evolved in said converters and separately withdrawing unconverted liquid oil from the converters.

25. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises forcing oil from a supply tank through a battery of converters independently and in flowing streams, independently heating the converters of the battery to cracking temperatures under superatmospheric pressures, to effect conversion of the oil in transit therethrough, separately removing the vapors evolved in the several converters and returning unconverted liquid oil from the several converters to the supply tank for retreatment.

26. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises independently charging oil in flowing streams through a battery of converters separately heated to cracking temperatures under superatmospheric pressures, equalizing the pressure in the several converters by maintaining free and open communication between the vapor spaces thereof, independently removing the evolved vapors from the several converters and delivering them to a common vapor line separately removing unconverted liquid oil from said converters and delivering it to a common oil line.

27. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises delivering oil from a supply tank to a battery of converters independently and passing the oil therethrough in flowing streams, independently heating the several converters to cracking temperatures under superatmospheric pressures, equalizing the pressures within the several converters by freely connecting the vapor spaces thereof, separately removing the evolved vapors from the several converters and subjecting them in common to condensation, independently withdrawing unconverted liquid oil from the several converters returning it to the supply tank for retreatment.

28. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises forcibly delivering oil from a supply tank to one end of a plurality of ver-

tical converter tubes and passing it therethrough in flowing streams to be cracked in transit, heating the converter tubes intermediate their ends to a cracking temperature under superatmospheric pressure, withdrawing unconverted liquid oil from the opposite ends of said vertical converter tubes and returning it to mix with the oil in said supply tank for retreatment and removing the vapors evolved in the converter tubes.

29. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises forcibly delivering oil from a supply tank to one end of a plurality of vertical converter tubes and passing it therethrough in flowing streams to be cracked in transit, heating the converter tubes intermediate their ends to a cracking temperature under superatmospheric pressure, withdrawing unverted liquid oil from the opposite ends of said vertical converter tubes and returning it to mix with the oil in said supply tank for retreatment, removing the vapors evolved in the converter tubes, and collecting below the heating zone carbon and heavy residue formed in said converter tubes and emerging from the lower ends thereof.

30. A process of converting high boiling hydrocarbon oil into lower boiling products that comprise forcibly delivering oil from a supply tank to one end of a plurality of vertical converter tubes and passing it therethrough in flowing streams to be cracked in transit, heating the converter tubes intermediate their ends to a cracking temperature under superatmospheric pressure, withdrawing unconverted liquid oil from the opposite ends of said vertical converter tubes and returning it to mix with the oil in said [fol. 1349] supply tank for retreatment, removing the vapors evolved in the converter tubes, collecting below the heating zone carbon and heavy residue formed in said converter tubes and emerging from the lower ends thereof, and supplying fresh oil to the system during the operation thereof to compensate for the removal of evolved vapors.

31. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises delivering oil from a supply tank to the upper ends of a plurality of vertical converter tubes, and forcibly passing it downwardly therethrough in flowing streams to assist the action of gravity in carrying carbon downwardly through said con-

verter tubes, heating the converter tubes intermediate their ends to a cracking temperature under superatmospheic pressure to convert the oil in transit, collecting below the heating zone carbon descending from the vertical converter tubes, returning unconverted oil from the lower ends of the converter tubes to the supply tank for retreatment and removing from the system the vapors evolved in said vertical converter tubes.

32. A process of converting high boiling hydrocarbon oil into lower boiling products that comprises delivering oil to one end of a plurality of vertical converter tubes and forcibly passing it under superatmospheric pressure therethrough in flowing streams to be cracked in transit, heating the vertical converter tubes intermediate their ends to a cracking temperature whereby the oil is converted in its passage therethrough, collecting carbon and heavy residue below the heating zone, withdrawing unconverted liquid oil from the exit ends of the vertical converter tubes and removing from the system the vapors evolved during the cracking operation.

In testimony whereof I affix my signature in the presence of two witnesses.

Joseph H. Adams.

Witnesses: A. Capstick, J. S. de Selding.

PETITIONER'S EXHIBIT 139

July 24, 1923. 1,462,678

J. H. ADAMS.

OIL CONVERTING APPARATUS

Filed June 15, 1916 5 Sheets-Sheet 1

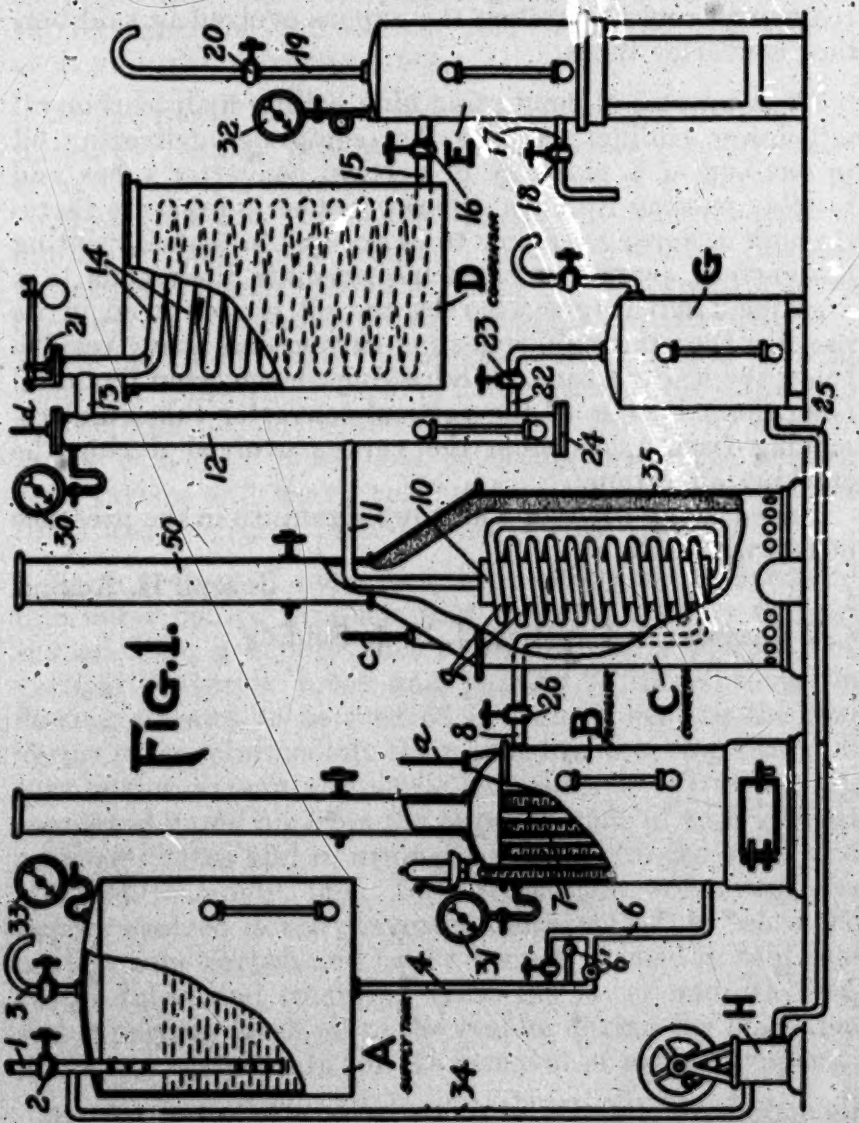


FIG. 1.

WITNESSES:

A. Capstick

Joseph de Selding

INVENTOR

Joseph H. Adams

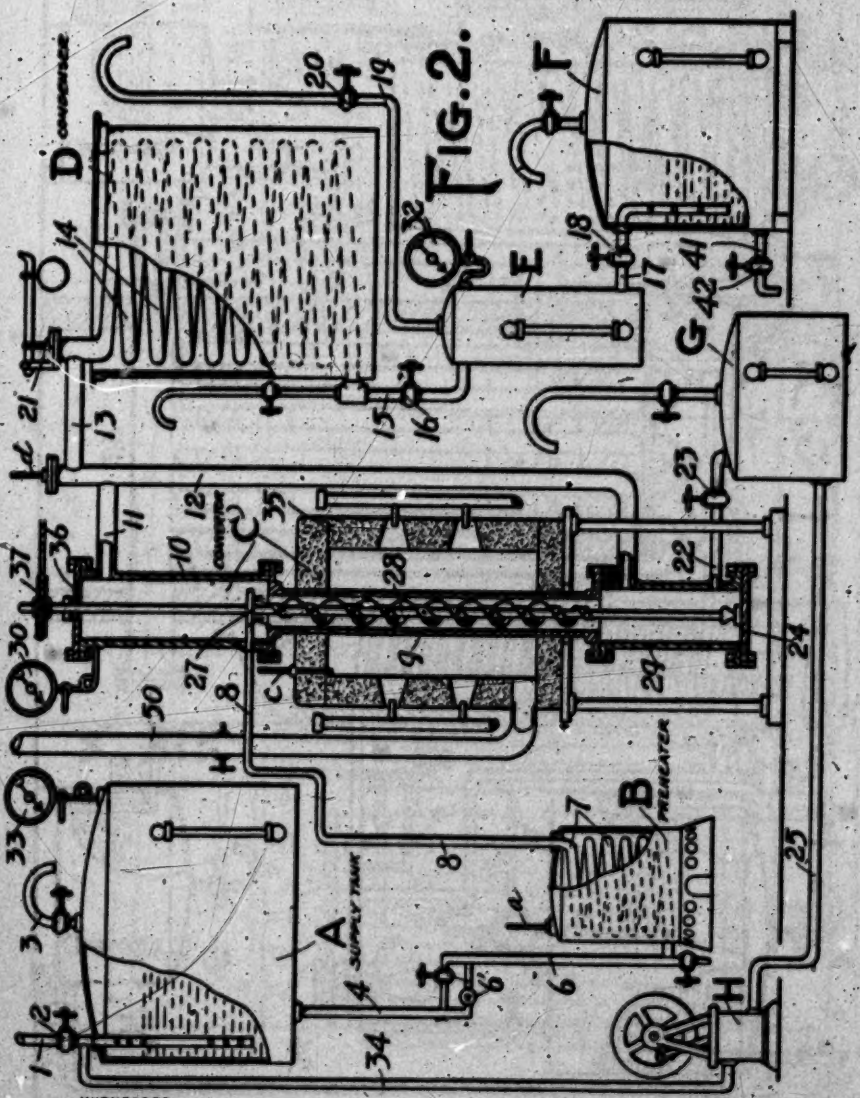
PX 139-1

[fol. 1351]

July 24, 1923. 1,462,678

J. H. ADAMS
OIL CONVERTING APPARATUS
Filed June 15, 1916 5 Sheets-Sheet 2

FIG. 2.



WITNESSES:
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Ex 199-2

4810

[fol. 1352]

July 24, 1923. 1,462,678

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OIL CONVERTING APPARATUS
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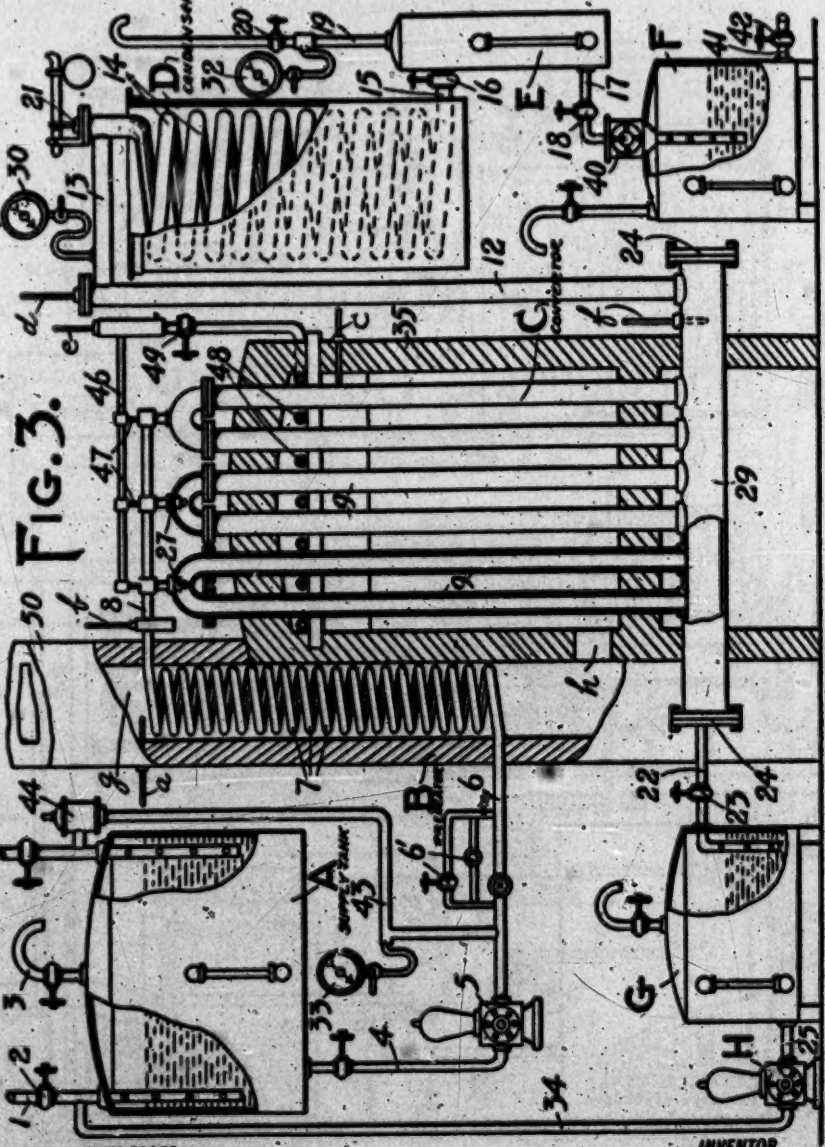

FIG. 3.

4811

[fol. 1353]

July 24, 1923

1,462,678

J. H. ADAMS

OIL CONVERTING APPARATUS

Filed June 15, 1916

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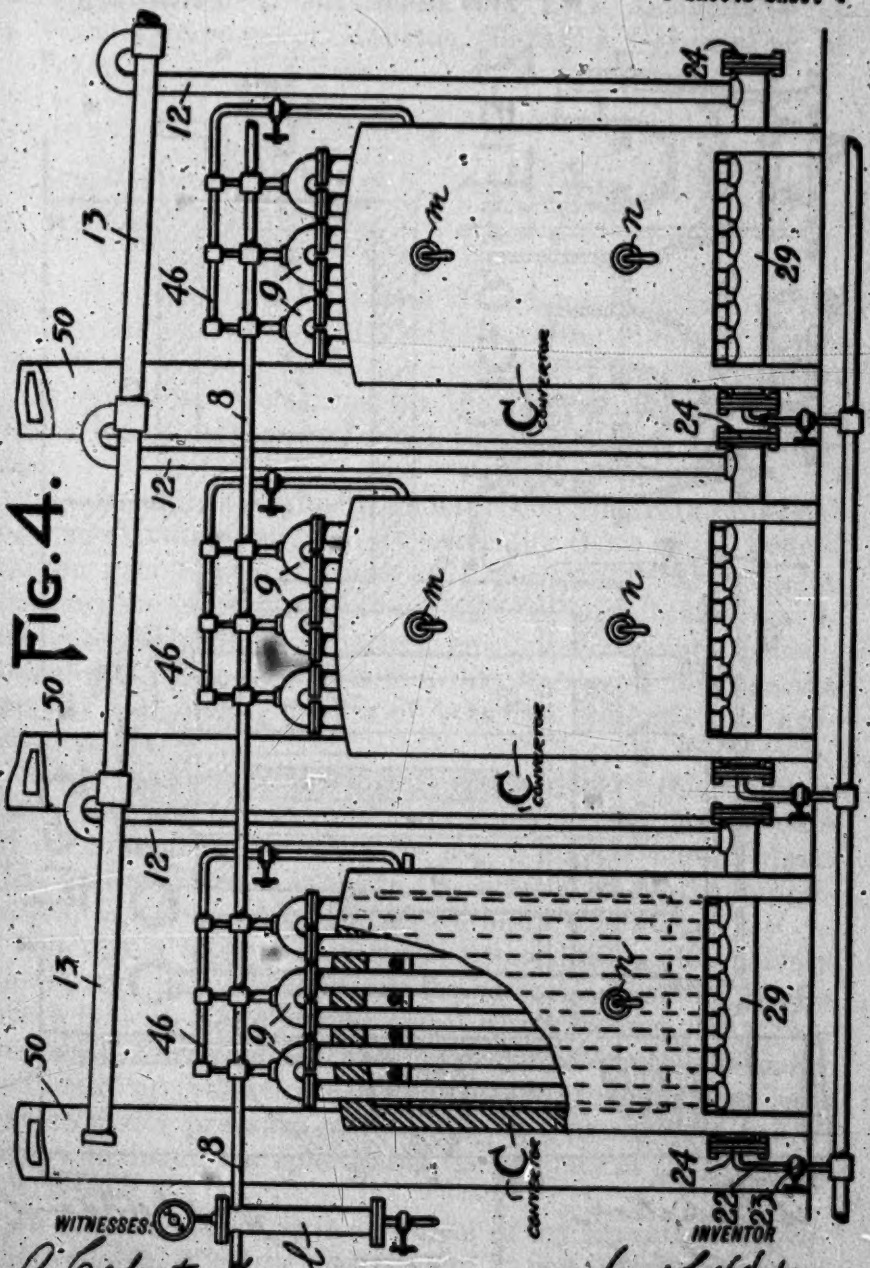

FIG. 4.

WITNESSES:

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INVENTOR

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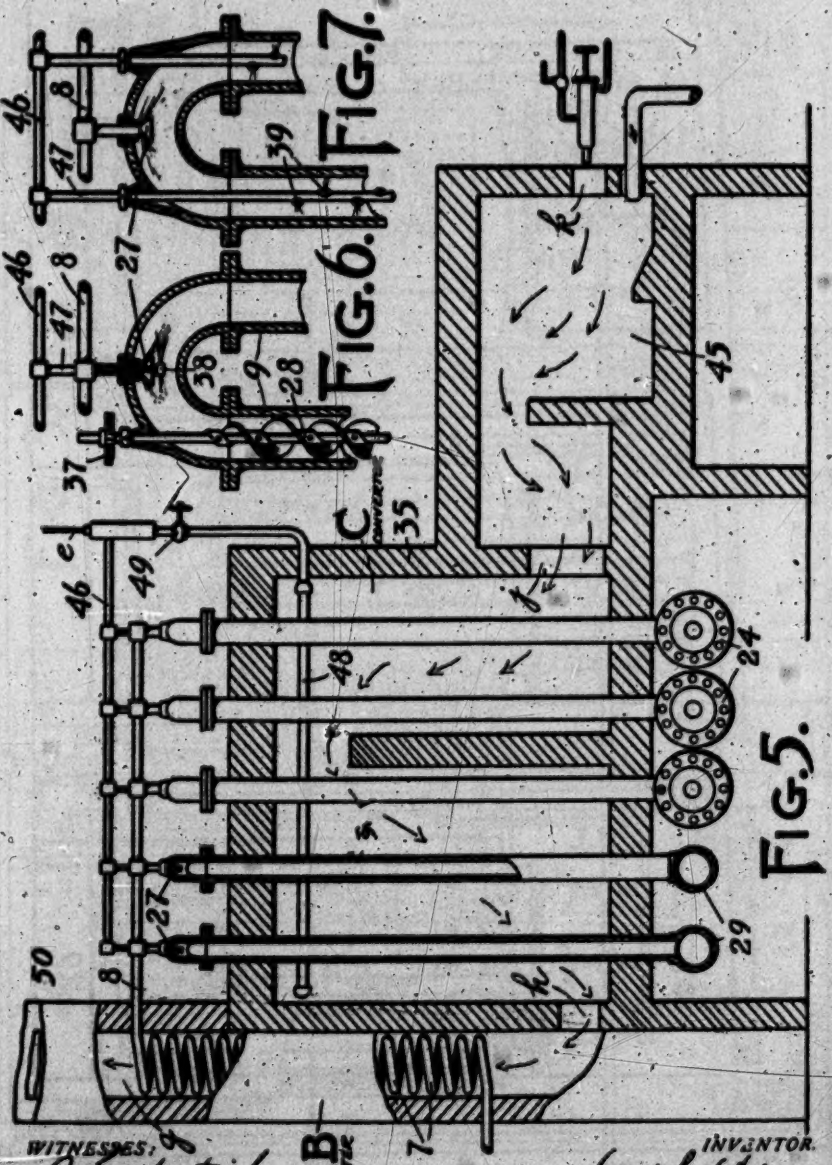
PX 149 4

4812

[fol. 1354]

July 24, 1923. 1,462,678

J. H. ADAMS
OIL CONVERTING APPARATUS
Filed June 15, 1916 5 Sheets-Sheet 5



[fol. 1355] Patented July 24, 1923. 1,462,678

United States Patent Office

Joseph H. Adams, of Flatbush, New York, Assignor to the Texas Company, of Houston, Texas, a Corporation of Texas

Oil-Converting Apparatus

Application filed June 15, 1916. Serial No. 103,726

To all whom it may concern:

Be it known that I, Joseph H. Adams, a citizen of the United States, residing at Flatbush, in the county of Kings and State of New York, have invented a new and useful Oil-Converting Apparatus for the Conversion and Transformation of Oils, and of which the following is a specification.

This invention relates to an improved apparatus for converting oils and liquids, more especially those of the hydrocarbon group into products of lower specific gravity for the purpose of obtaining from high boiling oils lower boiling products such as naphthas, gasolenes, benzines, benzol, toluol and other light oils and oily spirits of low specific gravity and boiling points of both the aliphatic and aromatic series.

While the apparatus which is the subject of this application is adapted to carry out in practical use a novel process of oil conversion invented by me, I do not herein claim that process since it is made the subject of another application, Serial No. 103,725 of even date herewith.

One object of my invention is to produce comparatively simple and inexpensive means for accomplishing the results above indicated and to that end it embodies means for preheating the original oils and volatilizing them while under self-built up vapor pressures, means for heating said vapors under pressure to cracking or converting temperatures and means for condensing the product of the cracking operation.

In another aspect, it is an object of my invention to provide reliable, effective and efficient vapor phase apparatus for commercially converting high boiling hydrocarbon oil into lower boiling products, and particularly to make pro-

vision for conserving the heat of the converter so that it shall be utilized substantially entirely for the actual cracking operation. The accomplishment of this end is attained by providing suitable means for initially preheating the oil under superatmospheric pressure to substantially its corresponding boiling or vaporizing point, the pressure being sufficient to maintain the heated oil in liquid form while and after it is thus raised in temperature. The highly preheated liquid oil, in a state of incipient vaporization, is then discharged or released into a converter which is maintained at a cracking temperature and at a superatmospheric self imposed vapor pressure somewhat less than the preheater pressure, whereupon the liberated heated oil expands and breaks into vaporous form, in which it is subjected to the full cracking heat of the converter and effectively cracked or converted in the vapor phase.

The apparatus is so constructed as to permit continuous operation since oil may be supplied continuously to the preheater and the hot oil continuously forced and sprayed into the converter and the converted vapors may continuously pass to the condenser.

These and other objects and novel features of the invention will be apparent from the following description taken in connection with the accompanying drawings of apparatus in which the same reference characters, whether in letters of the alphabet or numerals, will denote corresponding parts throughout the several elevation and sectional drawings of which:

Fig. 1, is an elevation and partly sectional drawing of a simple apparatus adapted for carrying out my process.

Fig. 2, is an elevation and partly sectional drawing of another and more complete apparatus embodying additional details.

Fig. 3, is a partly sectional elevation drawing of a commercial type of apparatus more complete in detail and structure.

Fig. 4, is an elevation drawing of a battery of vapor converters showing the free communication of the units one with another.

Fig. 5, is an elevation and partly sectional view of the heat exchanger for pre-heating ingoing oil, the combustion chamber of re-generative furnace and group of vertical vapor converting chambers enclosed within the body of the high temperature furnace.

Fig. 6, is a sectional drawing showing the manner of admitting super-heated steam to the oily vapors undergoing transformation and:

Fig. 7, illustrates another means of introducing superheated steam to the oily vapors while being subjected to the powerful influence of cracking heats and high vapor pressures.

In Fig. 1, of the drawings I have shown a simple form of [fol. 1356] apparatqus which embodies the main elements of my invention and in Fig. 2, I have shown the same broad features with changes and additions; while in Fig. 3, there is shown an apparatus capable of being operated on a commercial scale wherein the same broad features are amplified with additions in the nature of improvements or additional details.

In these three figures I have designated the main elements of the apparatus with letters of the alphabet whereas the specific parts are marked with reference numerals, the same reference characters being used to indicate corresponding parts in the three figures.

Referring particularly to the simple form of apparatus shown in Fig. 1, the reference character A, represents an oil supply tank from which the oil is supplied to the apparatus for the conversion process.

The oil passes from the tank A, through pipe 4, precision feed valve 6′ and pipe 6, to pre-heater B, in the coils or pipes 7 of which the oil is heated, then through pipe 8, to the tube coils 9 and chamber 10 of converter C, where the hot oil breaks into spray or mist like vapor so that in such gaseous form it may come in contact with cracking heats within the coils 9 and chamber 10.

The pre-heater B, is of any preferred construction, as a feed water heater, a small boiler or other form of heater, whereby the oil may be heated by suitable means in order to raise it in temperature to, or approaching, the boiling or vaporizing point so that when admitted or sprayed into the cracking chamber or tubes it will break into vaporous form.

The converter C, embodies an outer casing 35, of heat enduring and insulating material for confining the heat, and any suitable means may be provided for heating this chamber, such as fuel oil or gas burners or other economical means of fuel consumption.

I prefer making the converter itself in tubular form so that there will be a large heating surface presented as compared to the volume of vapor undergoing conversion passing through the converter; and in the form shown in Fig. 1, the converter C comprises a pipe coil 9 and an enlarged chamber 10. The oil, preheated under pressure to substantially its vaporization point at that pressure in the preheater B, is delivered through valve 26 in a thin stream into the bottom of the coil 9 through which it rises and is then admitted into the enlarged chamber 10. Both the coil 9 and the chamber 10 are heated to intense cracking temperatures which are in excess of the temperature of the preheater. Therefore, as the oil in a state of incipient vaporization, rises through the pipe 9 and into the enlarged chamber 10 the relation of heat to pressure is such that the oil in transit will break into and maintain a vaporous form in which it is cracked.

The vapors, after being subjected to the high temperatures in the coils 9 and the enlarged chamber 10, pass out through pipe 11, to separating chamber 12, where the lighter converted vapors rise and flow through pipe 13, to condenser D, where in the coils 14, the vapors are passed down and condensed to liquid; and, together with the fixed gases generated during the process, are drawn off through pipe 15 and valve 16, into running trap tank E, which is provided with a draw off pipe 17, controlled by valve 18.

It will be understood that the supply tank A, can be refilled from time to time through inlet pipe 1, and that the supply of oil from that tank to the converter C, may be augmented by compressed air pressure which is applied over the surface of oil in the tank in order to force it into the pre-heater B, and so on into the converter C, the valve 2, being closed as well as the valve in the vent pipe 3, and the air pressure being registered on pressure gauge 33.

The compressed air may be supplied from any suitable source (not shown) and may conveniently be introduced through the pipe 3 if desired. Sufficient pressure is thus maintained upon the supply of oil to force it through the preheater against the back pressure of the converter and to hold the heated oil in liquid form while being raised to substantially its corresponding boiling point and until it is introduced by releasing or spraying it into the converter in which it immediately vaporizes and is cracked.

The pre-heater B, is intended only to heat the oil sufficiently to cause its easy vaporization when admitted to the converting chamber or coils 9, through pipe 8, and is not intended to perform any cracking operation; the heated oils at the time of admission to the said chamber then being at a temperature sufficient to immediately vaporize and expand them for the vapor conversion process as carried on in this apparatus.

The temperature of the converter C, is raised to such a point as will crack or convert the oily vapors into lower boiling products or convert them into products having essentially different natures. By reason of the preheating of the oil to substantially its vaporization point, the heat of the converter is fully expended in effectively and efficiently cracking the oil in the vapor phase.

It will be seen that the condenser D, is in open communication with the converter C, through pipe 11 and separator 12, and therefore any pressure in the converter will extend to and through the condenser.

The continual feeding of new quantities of hot oil in liquid form to the apparatus, will build up or raise the [fol. 1357] vapor pressure in the converter; and consequently throughout the condenser, so that the vapors undergoing the cracking operation will at all times be under superatmospheric pressures while being subjected to cracking heats. This pressure is somewhat less than that utilized to force the oil through the preheater and against the back pressure of the converter.

This pressure maintained in the converter and through the condenser may be regulated by controlling the discharge of fixed gases which are always generated to a more or less extent in the converter.

The condensation of vapors also tends to reduce the pressure and thus control of the escape of fixed gases is sufficient to enable the operator to maintain the pressure desired.

The fixed gases pass out with the condensed vapors through the pipe 15, into the trap tank E, and their escape through the pipe 19, is controlled by valve 20.

When the apparatus is in operation, pressure in the converting system will be regulated by the valve 20 and registered on gauges 30 and 32, which latter, under normal operative conditions, should both indicate the same uni-

form pressure while for safety purposes in this high pressure system, comprising pre-heater B, converter C, condenser D and the running trap tank E, the release blow off valve 21, is provided and located about over the condenser D.

The gauges 30 and 32, register vapor pressures while in this form of apparatus gauge 31, on pre-heater B, registers the oil pressure which in all cases should be below the pressure maintained over the oil in supply tank A, as registered on gauge 33.

Vapors which pass out from the expansion chamber 10, through pipe 11, and into the separator column 12, may there be separated into the lighter ones, which pass to the condenser D, and heavier partially or wholly unconverted vapors which will drop to the bottom of the column together with particles of coke or carbon.

The bottom of this chamber 12, is connected to overflow hot oil tank G, by means of pipe 22, the flow of oil through which is regulated and governed by valve 23, and this column 12, is also provided with a detachable plate 24, so that solid or semi-solid matter and deposit may be removed from time to time.

The material collecting in the tank G may be returned to the supply tank for further treatment, the pump H serving to draw off the oil through the line 25 and return it to the tank A through the line 34.

The drawing Fig. 2, presents a partly sectional elevation of an apparatus adapted to carry out my process embodying a suitable oil supply tank A, and air pressure pump H, to maintain pressure over the surface of oil in the tank in order to force it into converter C, through pre-heater B, against a high back or vapor pressure while maintaining the oil in liquid form; a converter C, in tubular form enclosed within a high temperature furnace, 35, a condenser D, and liquid running trap E, in free communication with the converter, an enclosed running tank F, for the distillates of converted oils connected with the trap E, and tank G, for partly or wholly uncoverted oils which may be removed from time to time from the lower or heavy bottoms chamber 29, and returned through pipe 25 and pump H, to supply tank A, for retreatment.

With reference to the drawing Fig. 2, the source of supply or oil tank may be located at any distance from the pre-

heater B, and by means of compressed air maintained over the surface of oil in tank A, in excess of vapor back pressure in the system, the oil is delivered continuously into the converting tube under uniform pressure to replace that which is being withdrawn in vaporous form and condensed.

Original oil may be admitted to tank A, through pipe 1, regulated by valve 2, and displaced air may escape through pipe 3, when the tank is filled at first, but subsequently it must be forced in at greater pressure than that maintained by compressed air over the surface of contained oil.

It is best always to pre-heat original oil before admitting it to the vaporizing system so that the heat from the furnace may be conserved for the purposes of conversion and not for pre-heating it, and to this end waste heat from the furnace can be economically applied in an exchanger to the purpose of heating inflowing oil.

This method as carried out in the apparatus is shown in Fig. 3, where a pipe coil 7, is located in the flue *g*, of stack 50, and which, in the case of the apparatus shown in both Figs. 1 and 2, can be readily adapted to use in the exhaust heat stacks of the furnaces employed for the conversion of oily vapors.

The pre-heater B, may assume any convenient shape as a feed oil heater under pressure in which oils may be economically and rapidly heated nearly to their boiling points before spraying or discharging them in vaporous form into the converter.

The drawing Fig. 2, shows one of the many forms of tubular converters which may be employed in my apparatus for carrying on the oil conversion process referred to, and in this type of apparatus the tube 9, is constructed of material capable of withstanding intense temperatures and high pressures and enclosed within a furnace 35, composed of [fol. 1358] fire brick walls designed to withstand high cracking heats.

At the upper end of the tube 9, the enlarged chamber 10, permits the lighter converted vapors to become more or less separated from the heavier ones and pass out through the vapor pipe 11, to condenser D, while the heavier partially or wholly unconverted vapors drop back and down through the tube 9, for further treatment, while the very heavy ends as well as any carbon cracked out in mineral form may precipitate or fall into the heavy bottoms chamber 29, located below the tube.

This chamber 29, is connected to overflow oil tank G, by means of pipe 22, regulated by valve 23, and is provided with a detachable plate 24, so that solid matter may be removed at times as required. The products accumulating in the tank G may be withdrawn through the line 25 by the pump H and returned to the supply tank A through the line 34.

The heated oil is delivered by spraying it in at the upper end of cracking tube 9, through a perforated collar or circular nozzle 27, which, with its own heat and the intense temperature of the converter, drives the oil into a vapor or mist like condition ready for contact with the cracking heats while held under super-atmospheric pressure during the operation of the apparatus.

As the oily vapors pass down through the tube 9, a part or all of them are converted into lower boiling products and while some of them flow out through pipe 11, leading from the upper expansion chamber 10, others flow through pipe 12, leading from the lower or heavy bottoms chamber 29 and through the condenser D. This pipe connection furnishes free and open communication between the converter C and the condenser D and permits an equalization of pressure.

Any free carbon accumulating in the tube 9, or vertical pipe 12, may be carried down into heavy bottoms chamber 29, where it is swept by the oily vapors in their course through tube 9 and pipe 12.

As an added feature of importance in this vertical type of tubular converter a rotor 28, provided with a helical strip of metal attached in screw like position on the shaft can be employed to remove the accumulation of carbon in the tubular chamber 9.

The shaft, which extends through the cap 36, and is provided with a stuffing box and which has a bearing at the lower end in the detachable plate 24, of the heavy bottoms chamber 29, can be revolved by power applied to a sprocket wheel, 37, located a short distance above the cap 36, and driven by chain gear so that it will revolve and remove the carbon.

Any free carbon held in suspension in the cracked vapors or precipitated therefrom will drop into the heavy bottoms chamber 29, through tube 9 or pipe 12, so that vapors led into condenser D, may be in part or wholly freed from mineral carbon; and any carbon adhering to the inside of

the vertical tube may, by means of the revolving rotor 28, be nipped off and caused to drop into the chamber 29, below the tube.

Referring now to the drawing Fig. 3, the source of supply or oil tank A, may be located at any required distance from the pre-heater B, and by means of pump 5, the oil is delivered continuously into the tubes 9, of converter C, through the heating coils 7 and pipe 8, to replace that which is continually withdrawn from the converter in the form of vapors.

Pump 5, is provided to draw oil through pipe 4, and force it through precision valves 6', pipe 6, pre-heater coils 7 and pipe 8, into the top of converting tubes 9, of converter C.

It is best to pre-heat original oil before admitting it to the converters, as through the spray nozzles, so that the heat from the furnace may be conserved for the purpose of cracking the vapors of oils and not for pre-heating it to cracking temperature; and to this end the waste heat from the furnace as it escapes through flue *h*, into the throat *g*, of stack 50, can be economically applied in this form of exchanger to the purpose of heating original inflowing oil through pipe coils 7.

The oil so heated is forced into the tubes 9, of converter C, through pipe 8, which delivers it to the several spray nozzles 27, at the heads of the tube connections against a back or generated vapor pressure maintained in the tubes 9, and throughout the several following parts of the system comprising the carbon and vapor chamber 29, the tubes 14 of condenser D, running trap tank E, and the intervening vapor and liquid pipes 12 and 13, 15 and 17, valve 16 and both sight glasses and pressure gauges located on the apparatus.

This drawing Fig. 3, shows one of the many forms of tubular converters which may be employed in my process apparatus, and in this type of apparatus a multiple of heat enduring tubes 9, constructed of materials capable of withstanding high temperatures and high pressures are located vertically in the high temperatures furnace and enclosed within fire brick walls 35, designed to withstand protracted high temperatures and cracking heats.

These chambers or tubes 9, are connected into a header or heavy bottoms chamber 29, at their lower ends and are assembled in groups attached to each header 29, so that

the entire group composed of two or more headers may [fol. 1359] receive the greatest efficiency from the furnace heat which may be generated in a primary chamber and passed into this furnace of converter C, or the heat generated primarily in the furnace enclosure containing the tubes, as a matter of mechanical efficiency.

This feature of furnace arrangement is clearly shown in Fig. 5, and while it is not claimed by me as new, it is shown to illustrate the manner of placing tubes 9, as closely together as possible in order to present the greatest area of heats and heat currents generated in the fire box 45, or the principal chamber of converter C, which arrangement facilitates the efficiency of the process as carried on in this apparatus.

At the lower outgoing ends of the series of tubular chambers 9, vapors are led into a carbon and oil vapor trap, 29, where any free carbon accumulated during the process is swept by the current of oily vapors in the tubes.

This trap 29, is provided with detachable plates 24, at its ends for cleaning out purposes and leading from one or both ends of the chamber a vapor pipe 12, conducts light converted vapors to coils 14, of condenser D.

Any free carbon which may be held in suspension in vapors issuing from the converting tubes 9, may have a chance to precipitate to the bottom of this header or trap 29, and from vapor line 12, while vapors are rising therein so that vapors led into the condenser D, may be in part or wholly freed from mineral carbon.

Any oils or condensed vapors caught in the bottom of trap 29, may be intermittently or continuously withdrawn through pipe 22 and valve 23, into hot oil collecting tank G, from which they may be withdrawn through pipe 25, by pump H, and returned to oil supply tank A, through pipe 34, for re-treatment as before.

The vapor line 12, rising from one end of the chamber 29, conducts vapor into the coils or pipes 14, of condenser D, which latter may assume any of the forms employed in the oil refining industry.

The oils or pipes 14, of condensing apparatus D, are ordinarily immersed in cold water and the rapidity of condensation as well as the quality of product can be partially controlled by the temperature of the water surrounding these condensing oils or pipes.

Condensate accumulated in the condenser runs without interruption into an enclosed collecting or running trap tank E, freely connected therewith by pipe 15 and valve 16, from which it is withdrawn into running tank F, through pipe 17 and valve 18, after passing sight box 40.

Any accumulation of distillate in the tank F, may be drawn off through pipe 41 and valve 42, to make room for newly and continuously admitted distillates from trap tank E.

The vapor pressure is indicated and regulated as in the form shown in Fig. 1.

In feeding oil to the system through pump 5, pump cannot be so accurately regulated as to constantly deliver the required amount of oil into the converter chambers, therefore a return pipe 43 and enclosed pop or release valve 44, will permit any excess oil not delivered into the system to be returned to the supply tank A.

This pop valve 44, can be set at any tension ten to fifteen pounds or more greater than the pre-determined number of pounds pressure maintained in the system and with the pump 5, operating under normal conditions all oil not delivered through the precision valve 6', will be returned under pressure to the tank A, through the release valve 44, and such pressure may be constantly known and under observation by means of gauge 33, arranged in the excess oil line 43, so as to be constantly informed as to the conditions under which the pump 5, is working.

Thermometers and pyrometers, *a*, *b*, *c*, *d*, *e* and *f*, are placed at several important locations on the apparatus so that a comprehensive idea may be had as to the temperatures of heats, vapors, steam, etc.

A feature of primary importance in the invention is simplicity in the operative features of the apparatus as well as the rapid, continuous and safe method of oil and oily vapor transformation to produce large yields of low boiling hydro-carbons and other oily products.

The multiplicity of tubular converters present large surfaces to the furnace heats in proportion to the amount of oil in vapor form contained in the tubes, and thus the yield of light distillates will be rapid and the quality high in desired products.

A considerable number of tubes having a comparatively small diameter of from two to eight inches may be so ar-

ranged as to present from four to six times greater surfaces to the intense furnace heat than the parts of tubes extending through and beyond the furnace walls for terminal and return fittings, if such an arrangement is employed.

When the supply pump 5, is in operation oil will be constantly flowing under pressure through the coils 7, of preheater B, into the cracking chambers being admitted to said cracking chambers through spray nozzles 27. The spray or vapors take the place of those already converted and condensed.

This newly admitted oily spray or vapor will in turn be super-heated, cracked and sub-divided into finer vapors and changed in the apparatus into lighter or more volatile pro- [fol. 1360] ducts by splitting the molecules of or rearranging them and breaking out small portions of carbon.

In this manner the complex mixtures of of oily vapors through one or more of the fuel coal tar, creosote, rosin and others may be changed by means of my process in this apparatus into mixtures of lighter oils which bear a general resemblance to those which are commercially known as naphtha, gasolene, benzine, benzol, toluol, and other light oils and oily spirits.

It may here be mentioned that during the operation of the process in this apparatus the raw non-converted oils will be relieved of a percentage or small portion of mineral carbon which, due to the intense cracking heats, may assume the form of fine particles of coke and in this apparatus for oil transformation the chemical character of the vapors may possibly be changed from one or more of the products of the hydro-carbon series into others of an essentially different character and series.

The carbon which is removed in this manner will be in part deposited in the tubular converters and in part precipitated in the carbon and vapor trap 29, as the certain small portion broken out in the process may be held in suspension in the vapors during a part of their course through the converting tubes 9, and adjacent pipes and condensing tubes 14, of apparatus D.

The continual circulation of oily vapors through the tubes permits the intense heat to act rapidly and convert high percentages of the subjected vapors into desirable products and the small quantity of vapors contained within

such tubes, traps, cooling coils and vapor lines assures a certain degree of safety in the operation of this apparatus, for if a break should occur in any part of the converting system under pressure, the fire which might result would be confined principally to a very few barrels or gallons of oil in vapor form undergoing treatment rather than to the more destructive and dangerous fire resulting from a breaking of the still full of liquid oil.

The furnace of converter C, may be operated in any convenient manner with coal, fuel oil, gas, electricity or other economical and easily obtainable heat producing medium, but for uniformity of result, economy and generally satisfactory operation, a fuel oil burning equipment is, at the present time, and for general localities, the most practical method of generating intense temperatures such as are required in the furnace of this converter.

Almost any of the efficient oil burning systems are adapted to this work but as that part of the apparatus is not a feature of this invention any specific description is avoided beyond the indication of a burner projecting into the opening *k*, of the combustion chamber 45, of Fig. 5, the flues *j* and *h*, and in the location of the stack 50, rising from the side or rear of the converter C, for draught or vent purposes.

As a feature of safety in this high temperature and pressure process the release blow off valve 21, is preferably located at a distance away from the converter, usually at the end of the vapor line 13, just above the condenser D.

In commercial practice where it is desirable to convert oil on a large scale it will be necessary to employ a number of converters in the same plant and in that case they should be arranged in battery form and they should be so connected that the vapor pressure from each will be transmitted to the others thus operating all under the same pressure.

Any tendeney toward a drop in pressure in one converter will be compensated for by the pressure from the others and thus easier and more perfect regulation may be secured.

This arrangement is shown in Fig. 4, where a battery of converters C—C—C, are spaced apart the required distance for mechanical operation and the proper arrangement of

connecting pipes and pipe connections, the hot oil being forced through pipe 8, and delivered to the tubular converting chambers 9, in each of the converters.

The converted and transformed vapors pass out through traps 29, in the vapor line 12, leading to the condenser where they are reduced to distillates in the tubes 14.

As each one of the tubular converting units comprising the chambers 9, are freely connected with the vapor line 13, by means of the pipes 12, leading out from the top of traps 29, and this vapor line leads freely to and is in open communication with the condenser in which vapors are condensed under vapor pressures maintained throughout the converting system, it will be seen that two or more converters comprising a battery will be equalized in operative vapor pressure through the vapor line 13, or other vapor lines which may be employed to connect and compensate the several converters for the purpose of equalizing and maintaining uniform pressures in the vapors undergoing transformation in such battery of converters.

This unit battery feature and the freely connected converters one with another in its broadest aspect was first adopted by me and employed as described in my co-pending application Serial No. 530,852, filed Dec. 1, 1909, which matured on October 28, 1919, into Patent #1,320,354, and is claimed in Patent #1,433,519, which is a division of said patent and was granted on October 24, 1922.

[fol. 1361] As an added feature of importance in this apparatus adapted for oil vapor treatment I may also use super-heated steam injected while at elevated temperatures into the body of oily vapors through one or more of the tubular converters 9, as indicated by pipe 46 and jet 47, shown in Fig. 3, and on a larger scale in Figs. 6 and 7, the steam being generated outside the apparatus but may be super-heated to any degree in the superheating coils 48, of Fig. 3, and Fig. 5, by the heat generated within the furnace of converter C, to which coils it may be admitted from outside and controlled in its entry into the oily vapors by valve 49.

The pipe 47, employed for such admission of steam may be more clearly seen in Fig. 6, where one is shown projecting into the top of an oil inlet and return bend connecting two tubes, the steam flowing through pipe 46, and admitted

to the interior of the converters by pipe 47 and a small perforated jet 38, at the bottom of the pipe through which the super-heated and gaseous steam is forced under higher pressure than that maintained in the converting system.

As a matter of convenience and mechanical practicability, I may also introduce the steam into the tubes 9, by projecting the steam pipe or pipes 47, into the end of one or more tubes, as shown in Fig. 7, carrying it down a part of or all of the length of each tube and providing the pipe with suitable openings or jets 39, for the proper admission of steam, which same is controlled by valve 49.

I ordinarily super-heat the steam above 800 to 1000° F. and when admitted and mixed with oil and oily vapors it possesses advantages both in hydrogenating oils and reducing mineral carbon deposit while at the same time the resultant distillates are superior in odor and color, and I therefore intend that this feature may be employed in this apparatus as a matter of practical and mechanical convenience at such times as the operator may find it advisable to introduce the same for the purposes described.

I may also employ rotors 28, in these vertical tubes as shown at the left side of Fig. 6, and install them as shown in Fig. 2, for the principal object of removing carbon from the interior of the tubes 9.

Having filled the reservoir tank or source of supply A, with original oil to be converted the fires are started in the furnace of converter C. Oil is admitted into the converting chamber 9, in small sprayed or vaporized quantities continuously, and as it falls through the chambers, becomes super-heated and is withdrawn through pipe 12, into the condenser D, and any heavier unconverted liquid portions which fall into the chamber 29, are drawn off from time to time or continuously and returned by pump H, to the supply tank A, until the coil 7, in the preheater B, has been raised in temperature sufficient to bring the oil to substantially its boiling point under the pressure maintained in the preheater and the tubes are heated to vapor cracking temperatures which may be determined by the pyrometer installed in the system, and the vapor pressure in the converter and condenser begins to rise.

The temperatures should finally be sufficiently elevated to prevent condensation of vapors while contained in the tubes

and as soon as the tubes 9, are full of vapors and the temperature increases until it reaches the required cracking heat they are then maintained at that temperature which will render the best conversion results continuously while the vapors are held under vapor pressures.

In the operation of this apparatus some of the vapors will necessarily be changed to fixed gases and some of the vapors will not be converted but a large proportion will be converted into lower boiling products essentially different in nature from the original material.

When the products pass from the converting tubes 9, into the trap 29, some of the unconverted oils of high boiling point will condense and may be drawn off through pipe 22 and valve 23, while the converted vapors and fixed gases will rise through pipe 12, and pass into the coils 14, of the condenser D. The converted vapors are here condensed and pass off in liquid form into tank F, through pipe 17 and valve 18.

The fixed gases are carried off by pipe 19, and the valve 20, in that pipe may be so adjusted as to allow the escape of so much gas as will maintain the desired pressure in the converter and condenser.

Preferably the process as carried on in this apparatus is operated as a continuous one, oil being continuously supplied from tank A, through pre-heater B, to the converter C.

The operation of forcing or spraying the hot oil into the converter where it immediately vaporizes and the generated self-imposed pressure of the vapors due to the cracking operation tend, of course, to raise the pressure in the converter but this is compensated for by the condensation of the vapors in the condenser and the regulated escape of fixed gases and thus, even in the continuous operation, the pressure may be maintained at the number of pounds desired during the operation of the apparatus.

It will be understood by those skilled in the art that the temperature necessary in the pre-heater B, converter C, and the pressure of the vapors in the converter through the condenser will vary with the characteristics of the particular oil being treated and therefore it is not possible to state any definite figures which would be applicable to all oils. [fol. 1362] The operator may determine when he gets the proper temperature in the converter by the character of

the product coming from the condenser, and then manipulate the apparatus in such a manner as to insure the greatest yield of desirable product at the most economical operation of the temperatures and proper regulation of the pressures.

In operation the valves 18 and 23, in discharge pipes 17 and 22, having been closed the tubular converters 9, and freely connected condenser D, with coils or tubes 14, and tank E, are sealed; and as the cracking heat is increased in the furnace of converter C, the cracking of the vapors in the tubes creates an autogenous pressure in addition to the pressures produced by pumping into the converter the hot oil under pressure.

These pressures together with heats in excess of those required merely to hold vapors in suspension or in gaseous form bring about the required transformation of the oils undergoing treatment while held in vapor form. As the oil under pressure in the pre-heater B, is brought to the vaporizing point continually by passing through the coils 7, the pump 5, forces them into the converters 9, through the spray nozzles 27, to take the place of the converted and condensed vapors continually passing through and out of the cracking chambers.

Any partially or wholly unconverted vapors leaving the tubes 9, and entering the trap 29, may fall to the bottom of that trap, from which they may be collected and removed in the form of hot oil into the tank G, and returned to the supply tank A, through pump H, for recirculation as before.

Thus it will be seen that vapors of sprayed hot oil having been driven through the converter and condenser are caught in liquid form in the tank E, while maintained under built up vapor pressures throughout the system from the pump 5, to the valves 23 in pipe 22, and 18 in pipe 17, and the high temperature in the converter brings about transformation of oils while the same are held in vapor form under high pressure for the purpose of breaking up and converting the heavier molecules into lighter ones or for reducing high boiling oils to lower boiling products.

Since various minor changes could be made in constructional parts and method of operating them and as many different combinations of parts could be made without depart-

ing from the fundamental principles and principal features thereof, it is my intention that all matter contained in the above description or shown in the drawings are to be taken as illustrative and not in a limited sense.

The apparatus is believed to be broadly new, operating in a new way to secure new results and therefore the terms used in the following claims are not to be read in a limited sense but are to be construed broadly.

Having described my invention what I claim as new and desire to secure by Letters Patent is:

1. A vapor phase apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a vertical converter, means for preheating high boiling oil under superatmospheric pressure to substantially its corresponding boiling point while maintaining it in liquid form, means for conducting said heated liquid to said converter and spraying it into the top thereof in vaporous form, means for spraying steam into said converter concurrently with the heated oil, and means for heating said converter to a cracking temperature and maintaining a superatmospheric pressure therein.

2. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising an oil supply tank, a preheater for raising the oil to substantially its boiling point, connections from said tank to said preheater, a furnace, a converter connected to said preheater and comprising a series of converter tubes contained within the furnace, and heated to cracking temperatures, a carbon-collecting chamber freely connected to said converter tubes, a condenser connected to said chamber, an enclosed running trap tank disposed beyond said condenser in free communication therewith, means for forcibly supplying hot oil through said pre-heater to said converter tubes in spray or vaporous form while the vapors therein are under high pressure and means for withdrawing partly or wholly unconverted oil from said carbon collecting chamber and returning it to said oil supply tank for retreatment.

3. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising an oil supply tank, a preheater for heating the oil, pipe connections between said tank and preheater, a furnace, a converter con-

nected to said preheater and comprising a series of converter tubes disposed within said furnace and heated to cracking temperatures, a pressure pump in said connections for supplying oil through said preheater to said converter, a spraying device for breaking hot oils into fine spray or vapors against a back pressure maintained in the converter tubes, a carbon-collecting chamber connected to the discharge ends of said converter tubes, a condenser connected to the vapor space of said carbon-collecting chamber, means for controlling the discharge of liquid and gases from said condenser and for maintaining vapor pressure in said converter and through said condenser.

4. Apparatus for converting high boiling hydrocarbon oil [fol. 1363] into lower boiling products comprising an oil supply tank, a preheater for heating the oil, pipe connections between said tank and preheater, a furnace, a converter connected to said preheater comprising a series of converter tubes enclosed within said furnace and heated to cracking temperatures, a carbon-collecting chamber connected to the discharge ends of said converter, a condenser connected to the vapor space of said carbon-collecting chamber, means for controlling the discharge of liquid and gases from said condenser and for maintaining vapor pressure in said converter and through said condenser and means for withdrawing from said carbon-collecting chamber the partially or wholly unconverted oil and returning it to the supply tank for retreatment.

5. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a supply tank, a preheater for heating the oil to substantially its boiling point, a furnace, a converter connected to said preheater and disposed in said furnace, means for superheating steam, means for discharging superheated steam into said converter, a condenser in free communication with said converter, means for continuously withdrawing oil from said supply tank and positively forcing it under pressure through said preheater and into said converter, means for breaking up the hot oils into spray or vaporous form for conversion, and means for maintaining vapor pressure in the converter and through the condenser.

6. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising an oil supply tank, a furnace, a converter connected to said supply tank and comprising a plurality of vertical converter tubes contained within the furnace and heated to cracking temperatures, a carbon-collecting chamber connected to the lower ends of said converter tubes, means for forcibly supplying oil to the upper ends of said converter tubes, means for maintaining superatmospheric pressure throughout said converter tubes and carbon-collecting chamber, means for removing from said chamber the vapors evolved in the converter tubes, and means for withdrawing unconverted liquid oil from said chamber and returning it to the supply tank for retreatment.

7. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a supply tank, a furnace, a plurality of vertical converter tubes extending therethrough and heated to cracking temperatures, a carbon-collecting chamber connected to the lower ends of said converter tubes, means for forcibly delivering oil from said supply tank to the upper ends of said cracking tubes, a condenser connected to the carbon-collecting chamber for receiving and condensing the evolved vapors and means for maintaining superatmospheric vapor pressure throughout the converter tubes, carbon-collecting chamber and condenser.

8. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a supply tank, a furnace, a plurality of vertical converter tubes extending therethrough and heated to cracking temperatures, a carbon-collecting chamber connected to the lower ends of said converter tubes, means for delivering oil from said supply tank to the upper ends of the converter tubes, a condenser connected to the carbon-colllecting chamber for receiving and condensing the evolved vapors, means for maintaining superatmospheric vapor pressures throughout the converter tubes, carbon chamber and condenser, means for withdrawing the unconverted liquid oil from said carbon chamber and returning it to the supply tank for retreatment, and means for permitting removal of carbon from said chamber.

9. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a vertically disposed converter, a furnace for heating the converter intermediate its ends to a cracking temperature, a preheater for heating oil under pressure to substantially its boiling point, means for forcing oil through the preheater and delivering it into the upper end of the converter in sprayed or vapor form, means for delivering superheated steam into the upper end of the converter in commingled relation with the sprayed oil, a condenser in free communication with the converter, means connected to the converter and disposed below the heating zone for collecting carbon gravitating from the converter, and means for maintaining superatmospheric pressure throughout the preheater, converter and condenser.

10. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a battery of separate converters independently heated to cracking temperatures, means for independently forcing oil in flowing streams through said converters to be cracked in transit, means for maintaining superatmospheric pressure in said converters, means for independently removing the vapors evolved therein and a common vapor line for receiving all of the evolved vapors and freely connected to the several converters to equalize the pressures maintained therein.

11. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a battery of converters independently heated to cracking temperatures, means for independently charging oil through said converters in flowing streams, to be cracked in transit, means [fol. 1364] for independently withdrawing the vapors evolved therein, means for maintaining equalized superatmospheric pressures in said converters and means for independently and separately withdrawing unconverted liquid oil and carbon therefrom.

12. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a battery of converters independently heated to cracking temperatures and adapted to convert oil therein under pressure, means for

passing oil through the several converters independently in flowing streams whereby it is cracked in transit, a common line for cracked product, means for delivering the cracked products from the several converters into said common line in free and open communication with the several converters, and means for maintaining superatmospheric pressure throughout said system.

13. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a plurality of furnaces, a battery of converters severally associated therewith and independently heated thereby to cracking temperatures under superatmospheric vapor pressure and through which oil under treatment is continuously and independently passed in flowing streams and cracked in transit, and means for freely converting the vapor spaces of said converters to equalize the vapor pressures therein and remove the evolved vapors therefrom.

14. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising an oil supply tank, a battery of converters independently heated to cracking temperatures, means for forcing oil from the supply tank through the several converters independently in flowing streams, means for returning unconverted liquid oil from the several converters to the supply tank for retreatment, means for maintaing superatmospheric pressure in the several converters and means for separately removing from said converters the vapors evolved therein.

15. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a battery of converters independently heated to cracking temperatures, means for delivering oil independently to said converters, means for independently removing the evolved vapors from the several converters, a common vapor line freely connected to the several converters for receiving said vapors and maintaining equalized superatmospheric pressures throughout said converters, carbon and residue chambers severally connected to the respective converters, means for separately removing unconverted liquid oil from said chambers, and a common oil line into which the unconverted oil from the several chambers is discharged, and

means for separately withdrawing carbon from said chambers.

16. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a battery of converters independently heated to cracking temperatures, means for delivering oil independently to said converters, means for independently removing the evolved vapors from the several converters, a common vapor line freely connected to said converters for receiving said vapors, and maintaining equalized superatmospheric pressures throughout said converetrs, means for removing unconverted liquid oil from said converters, a common oil line into which the unconverted oil from the several converters is discharged, a supply tank, connections from said supply tank to the oil delivering means and to the common liquid oil line and means in said connections for forcing oil from the supply tank through the several converters independently and for returning unconverted liquid oil to the supply tank.

17. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a plurality of series of vertically disposed converter tubes, a plurality of furnaces for severally heating the respective series of converter tubes, intermediate their ends to cracking temperatures, means for delivering oil continuously to the upper ends of the converted tubes of each series, carbon-collecting chambers connected to the lower ends of the tubes of each series, means for withdrawing liquid oil from the several carbon collecting chambers, a common vapor line, and vapor connections from the several series of converter tubes to said common vapor line for delivering the evolved vapors to said vapor line and for equalizing the pressures developed in the several series of converter tubes.

18. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a plurality of vertically disposed converter tubes located therein and heated to cracking temperatures under super-atmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, a supply

tank outside said furnace, means for forcibly delivering oil from the supply tank to one end of said vertical converter tubes and passing it therethrough in flowing streams whereby it is cracked in transit, means for withdrawing unconverted liquid oil from the opposite ends of said converter tubes and returning it to mix with the oil in said supply tank for retreatment and means for removing the vapors evolved in said converter tubes.

19. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a [fol. 1365] plurality of vertically disposed converter tubes located therein and heated to a cracking temperature under superatmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, means for interconnecting the upper ends of said converter tubes above the heating zone, means for interconnecting the lower ends of the converter tubes below the heating zone, a supply tank outside said furnace, means for forcibly delivering oil from the supply tank to one of said intreconnecting means whereby the oil is passed through said vertical converter tubes in flowing streams and cracked in transit, means for removing unconverted liquid oil from the other interconnecting means and returning it to the supply tank to be mixed with the oil therein and retreated, and means for removing the vapors evolved in transit through said converter tubes.

20. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a plurality of vertically disposed converter tubes located therein and heated to a cracking temperature under superatmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, a supply tank outside said furnace, means for forcibly delivering oil from the supply tank to one end of the vertical converter tubes and passing it therethrough in flowing streams whereby it is cracked in transit, means connected to the opposite ends of said converter tubes for returning unconverted liquid oil to said supply tank to be mixed with the oil therein and retreated, a chamber connected to the lower ends of said vertical converter tubes below the heating zone for collecting carbon and heavy residue formed

in said converter tubes; and means for removing the vapors evolved in the converter tubes.

21. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a plurality of vertically disposed converter tubes located therein and heated to a cracking temperature under superatmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, a supply tank outside said furnace, means for forcibly delivering oil from the supply tank to one end of the vertical converter tubes and passing it therethrough in flowing streams whereby it is cracked in transit, means connected to the opposite ends of said converter tubes for returning unconverted liquid oil to said supply tank to be mixed with the oil therein and retreated, a chamber connected to the lower ends of said vertical converter tubes below the heating zone for collecting carbon and heavy residue formed in said converter tubes, means for withdrawing carbon and heavy residue from said chamber, means for supplying fresh oil to the system during the operation thereof, and means for removing from the system the vapors evolved in the converter tubes.

22. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a plurality of vertically disposed converter tubes located therein and heated to a cracking temperature under superatmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, a supply tank outside said furnace, means for interconnecting the upper ends of said converter tubes above the heating zone, a carbon-collecting chamber connected to the lower ends of the converter tubes below the heating zone, means for delivering oil from the supply tank to said upper interconnecting means and passing it downwardly through the vertical converter tubes in flowing streams to be cracked in transit therethrough and whereby the action of gravity is assisted by the downward flow in carrying carbon downwardly into the carbon collecting chamber, means for returning unconverted liquid oil from the said chamber to said supply tank for retreatment, and means for removing from the system the vapors evolved in said converter tubes.

23. Apparatus for converting high boiling hydrocarbon oil into lower boiling products comprising a furnace, a plurality of vertically disposed converter tubes located therein and heated to a cracking temperature under superatmospheric pressure and having their respective ends projecting through the upper and lower walls thereof, means for delivering oil to said vertical converter tubes and forcibly passing it under pressure in flowing streams therethrough whereby it is converted in transit, means for conducting off the unconverted liquid oil emerging from the converter tubes, a chamber connected to the lower ends of said vertical converter tubes for receiving the carbon and heavy residue formed in said converter tubes, means for removing carbon and heavy residue from said chamber, and means for withdrawing from the system the vapors evolved in said converter tubes.

In testimony whereof I affix my signature in the presence of two witnesses.

Joseph H. Adams.

Witnesses: A. Capstick, J. S. de Selding.

[fol. 1366] **PETITIONER'S EXHIBIT 227**

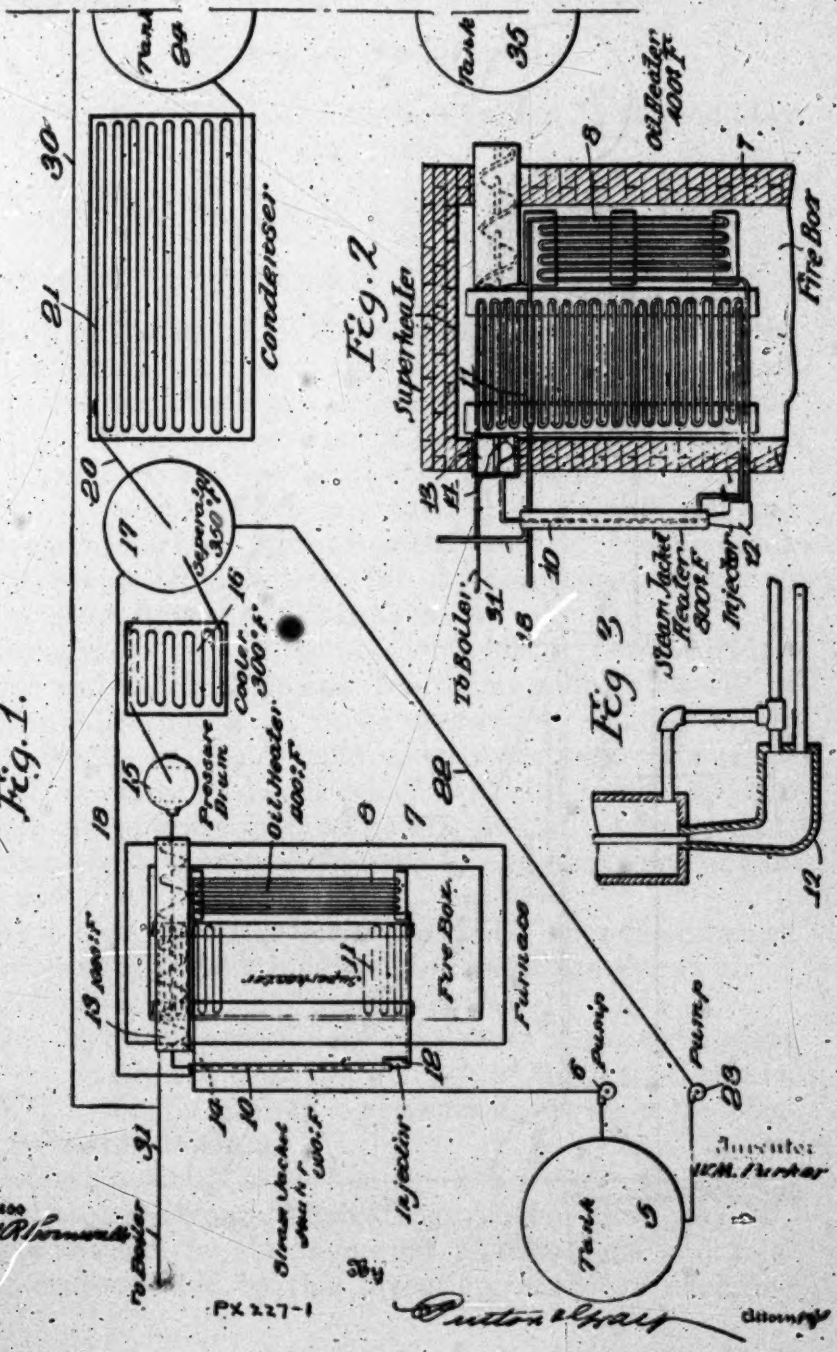
W. M. PARKER.

PROCESS FOR REFINING OILS.

APPLICATION FILED APR. 4, 1916.

1,226,990. **Patented May 22, 1917.**

2 SHEETS—SHEET 1.



4840

[fol. 1367]

W. M. PARKER.

PROCESS FOR REFINING OILS.

APPLICATION FILED APR. 4, 1916.

1,226,990.

Patented May 22, 1917.

2 SHEETS—SHEET 2.

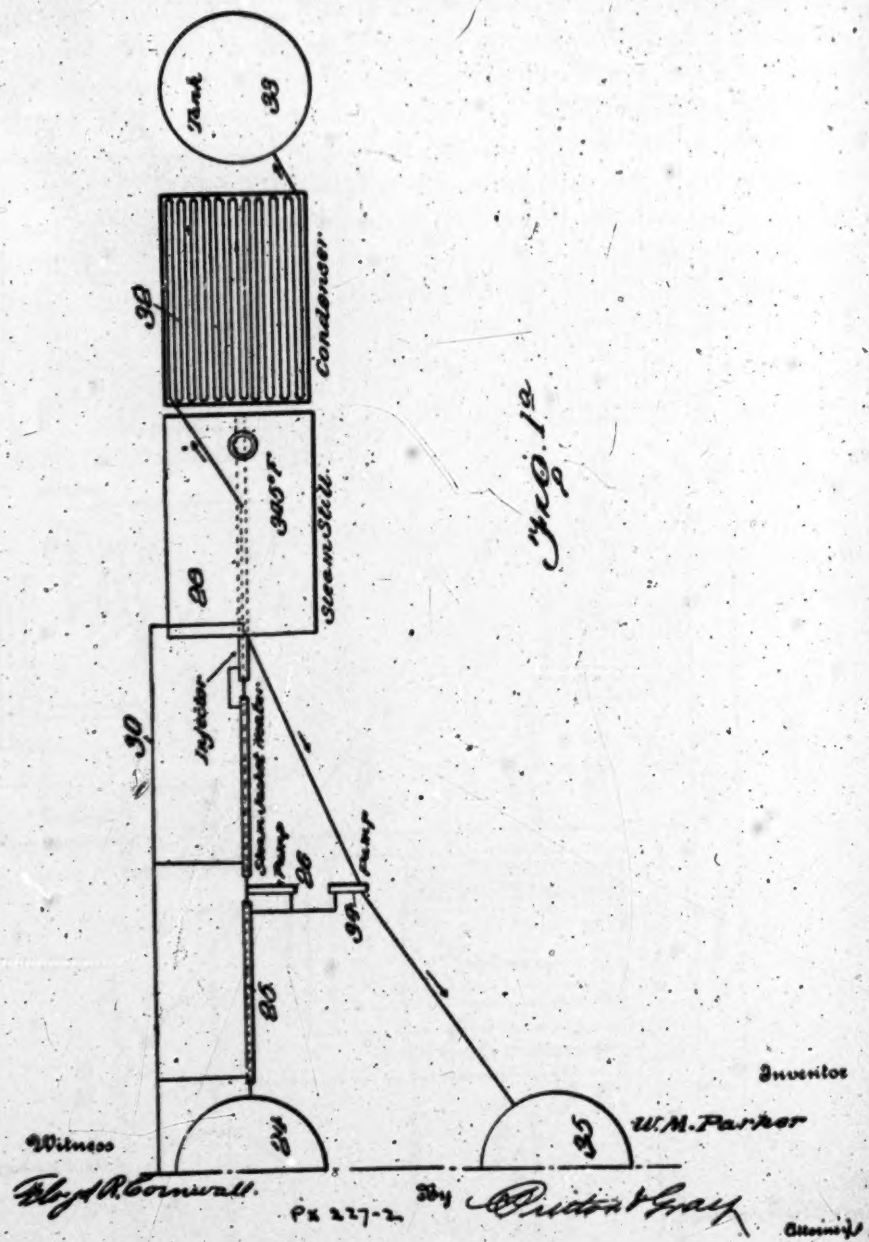


Fig. 1a

Pat 227-2

[fol. 1368] United States Patent Office

William M. Parker, of Oklahoma, Oklahoma, Assignor, by Mesne Assignments, to Parker Process Company, a Corporation of Delaware

Process for Refining Oils

1,226,990. Specification of Letters Patent. Patented May 22, 1917

Application Filed April 4, 1916. Serial No. 88922.

To all whom it may concern:

Be it known that I, William M. Parker, a citizen of the United States, residing at Oklahoma City, in the county of Oklahoma and State of Oklahoma, have invented certain new and useful Improvements in Processes for Refining Oil, of which the following is a specification.

This invention relates to a process of refining oils and more particularly to a process of refining or treating crude petroleum or oil distillates for the purpose of obtaining one or more lighter oils therefrom.

One of the objects of the present invention is to provide a simple and practical process for refining oil which will be substantially continuous in its operation. Another object is to provide an efficient and inexpensive process of treating or refining crude oil which will divide the oil into lighter oils of more uniform quality and of larger percentage in quantity than are obtained by processes now in general use.

Other objects will be in part obvious from the annexed drawings and in part indicated in connection therewith by the following analysis of this invention.

This invention accordingly consists in the several steps and the relation of each step to each of the several others, both individually and in combination, all as more completely outlined herein.

To enable others skilled in the art so fully to comprehend the underlying features thereof that they may embody the same by the numerous modifications and relations contemplated by this invention, drawings depicting

a preferred form of the apparatus by which the process may be carried out have been annexed as a part of this disclosure, and in such drawings.

Figure 1 illustrates diagrammatically the first half of an apparatus which may be used in carrying out the present process;

Fig. 1ª is a similar view showing the last half of the same apparatus;

Fig. 2 is an enlarged view of a portion of the apparatus shown in Fig. 1 and,

Fig. 3 an enlarged view of the injector for the injection of superheated steam into the oil conduit.

In order that a clearer perception of the present invention may be had and the objects sought to be obtained thereby, it may be stated in brief that the present process breaks down the heavier oils into one or more lighter oils by subjecting said heavy oils to a series of high temperatures and pressures and passing them through the apparatus at a relatively high rate of speed as by means of a force pump, thereby materially departing from such processes now in general use based largely upon the fractional distillation methods.

Referring now to the drawings in which the apparatus is shown diagrammatically, there is provided a main supply tank 5 having an outlet to which is connected a pump 6 adapted to force the crude oil into a furnace or retort 7. This retort is provided at one side with a heating coil 8 of relatively small diameter piping and comparatively great length, preferably of one inch diameter and one hundred and fifty feet in length, through which the crude oil is rapidly forced by the pump 6 and exposed to a temperature of about 400° to 450° F. from whence it passes under approximately 100 pounds pressure to a jacketed heater 10 which is maintained at a temperature of about 800° to 900° F. by means of superheated steam produced by coils 11 within the retort 7. It is to be noted that prior to the entrance of the oil from the coil 8 to the jacketed heater 10 a small part, approximately 10%, of superheated steam is injected into the oil conduit at the injector 12 which materially aids in increasing the temperature to the desired point as it passes through the jacket.

After leaving the jacketed heater 10 the oil is passed through an expansion drum 13 provided with a spiral or helix 14 adapted to give the oil a whirling centrifugal and rectilinear movement. In other words, the oil which is really in the form of a vapor, due to the high pressure and temperature to which it is subjected, is forced to circulate or rotate very rapidly and as it is traveling at the rate of approximately 100 feet per second, the heavier parts of the vapor are forced outwardly from the center of the conveyor and exposed to the hottest temperature within the retort 7. The gas or lighter parts of the vapor stay nearer the center of the screw or helix and consequently a more uniform breaking of the oil as it passes through the member 13 will result, thus making a very [fol. 1369] much larger percentage of light gas from raw oils than if said oils were simply passed through pipes or heated in a still. From the expansion drum 13 the fluid mass passes to a pressure drum 15 where all carbon and deposits are allowed to settle before the fluid continues to a cooler 16 where the temperature is reduced to approximately 300° F.

After leaving the coil within the cooler the oil, gas and vapor obtained from the original oil passes to a separator 7 which is heated by superheated steam entering through the pipe 18 connected with the upper end of the steam jacket 10. At this point the temperature is raised to approximately 350° F. and all oil that will vaporize at this temperature passes through a pipe 20 to a condensing coil 21 maintained at a temperature of approximately 350° F. All of the oil that will not vaporize at this higher temperature is pumped from the separator 17 through pipe 22 by means of pump 23 back to the tank 5 where it is again forced through these steps of the process.

The oil, or benzin as it now may be called, is delivered from the condenser 21 to a temporary tank 24, thence forced rapidly through a steam jacketed heater, 25, Fig. 1ª, by means of steam pump 26, then through a second steam jacketed heater 27 into a steam still 28 maintained at a temperature of approximately 345° F. by means of steam admitted thereto by pipe 30 which connects with the pipe 31 leading from the superheater coils within the retort 7. All oil vaporizing at 345° F. passes from this still to a condenser 32 and thence into storage tank 33. Any residue

remaining in the still 28 is drawn off by means of pump 34 and delivered to tank 35 from which point it may be drawn off and passed through the first or second steps again, as desired.

It is of course to be understood that the apparatus which is shown largely diagrammatic is provided with the necessary valves, pyrometers, controlling and power means as may be necessary to effectively and continuously carry on the process; for instance the pumps may be economically driven by steam from the system shown.

From the above description, it will be seen that the process relates largely to a method of breaking down the heavy oils into lighter ones by subjecting the oils to a relatively high temperature and pressure as well as to a centrifugal motion while moving at a high rate of speed. The heavy oils are first put through a superheater and heated to the vaporizing point and thence conducted to a helical drum or conveyer within the furnace or retort where they are exposed to a much higher temperature according to the vaporizing point of the raw oils. As it passes through the drum as above explained the heavier portions are forced by the centrifugal action to the outer surface of the drum, where they are subjected to the highest temperature. If all of the oil were simply passed through a series of pipes or heated in a still, it would be necessary to raise the temperature to such a high degree that a large part of the oil would carbonize. This objection is avoided by the present process in which no carbon results, and only such parts of the oil that will stand the heat are subjected to high temperatures.

The present invention is therefore believed to be simple and practical in operation, reliable and highly efficient in use and inexpensive to carry out. In fact, the invention is believed to accomplish, among others, all of the objects and possess all the advantages herein set forth.

Without further analysis, the foregoing will so fully reveal the gist of this invention that others can be applying current knowledge readily adapt it for various applications without omitting certain features that, from the standpoint of the prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention, and therefore such adaptations should and are intended to be comprehended within the meaning and range of equivalency of the following claims.

I claim:

1. The herein described method of treating oil which includes the step of vaporizing oil at a temperature of approximately 1000° F. and simultaneously causing said oil to traverse a helical path at the rate of not less than approximately 100 feet a second.

2. The herein described method of treating oil which consists in the steps of heating the oil to approximately 400° F., mixing the same with a small per cent. of steam, at high pressure and subsequently exposing the mixture to a temperature in the neighborhood of 1000° F. while being simultaneously subjected to a whirling and rectilinear movement at a rate of speed not less than approximately one hundred feet per second.

3. The herein described method of treating oil which consists in the steps of heating the oil to approximately 400° F., mixing the same with a small per cent. of steam, exposing the mixture to a temperature in the neighborhood of 1000° F. and simultaneously subjecting the mixture to a rotative rectilinear movement under high pressure whereby the mixture travels through a helical rectilinear path at not less than approximately 100 feet a second.

4. The herein described method of treating oil which consists in the steps of forcing oil under relatively high pressure rapidly through a coil heated to approximately 400° F., subsequently increasing the temperature of the oil [fol. 1370] to approximately 1000° F. and while still under great pressure, forcing the oil vaporized at that temperature through an elongated helical drum at a rate of speed not less than approximately one hundred feet per second.

5. The herein described method of treating oil which consists in forcing the oil rapidly through a coil heated to approximately 400° F. and subsequently increasing the temperature to above 1000° F. to vaporize the oil and simultaneously forcing the oil vapor in a helical rectilinear path at not less than approximately 100 feet a second, allowing the oil vapor to cool and settle prior to a re-heating at a temperature of approximately 350° F., at which point the volatilizable and non-volatilizable oils are separated.

6. The herein described method of treating oil which consists in heating the oil to approximately 400° F., mixing the

oil with a small per cent. of steam, giving the mixture a helical rectilinear movement under high pressure and at a speed not less than approximately one hundred feet per second through a helical drum heated to about 1000° F., conducting the vapors to a condenser, and subsequently conducting the non-vaporizing oil back to the starting point.

7. The herein described method of treating oil which consists in heating the oil to a vaporizing temperature while simultaneously being subjected to a helical rectilinear movement under great pressure and at a speed not less that approximately one hundred feet per second, allowing the oil vaporized at a definite temperature to pass into a condenser, conducting the non-vaporized oils back to the starting point, collecting the condensed vaporized oils and reheating them to approximately 345° F. in a still which permits the volatilized oils to be collected in a condenser and the non-volatilized oils to be conducted to a point for re-treatment.

8. The herein described method of treating oil which consists in passing the oil through a coil within a retort heated to approximately 400° F., mixing the heated oil with approximately 10% of superheated steam at approximately 100 pounds pressure, heating said mixture to a point above 1000° F. subsequently subjecting the mixture to a very rapid rectilinear and helical movement and at a speed not less than approximately one hundred feet per second, passing the vapors to a pressure drum where the mixture is allowed to settle, separating the vaporizable oils from the non-vaporizable oils, and treating the former to a fractional distillation step while the latter is returned to the starting point.

9. The herein described method of treating oil which consists in forcing oil through a relatively small pipe at great speed and exposing the same to a temperature of approximately 400° F., adding a small per cent. of superheated steam and subsequently heating said mixture in an expansion drum to approximately 1000° F. whereby the mixture is vaporized, subsequently forcing said vapors in a helical rectilinear path and at a speed not less than approximately one hundred feet per second, cooling and then re-heating the vapors to a critical point at which tempera-

ture the vaporizable oils are thence conducted through a fractional distillation step while the non-vaporizable oils are returned for treatment.

In testimony whereof I affix my signature in presence of two witnesses.

William M. Parker.

Witnesses: M. H. Waters, C. E. Sanders.

4848

[fol. 1371]

PETITIONER'S EXHIBIT 228

E. HOLMES.

PROCESS OF AND APPARATUS FOR PRODUCING LIGHT HYDROCARBONS.

APPLICATION FILED AUG. 31, 1915.

1,241,979.

Patented Oct. 2, 1917.

2 SHEETS—SHEET 1

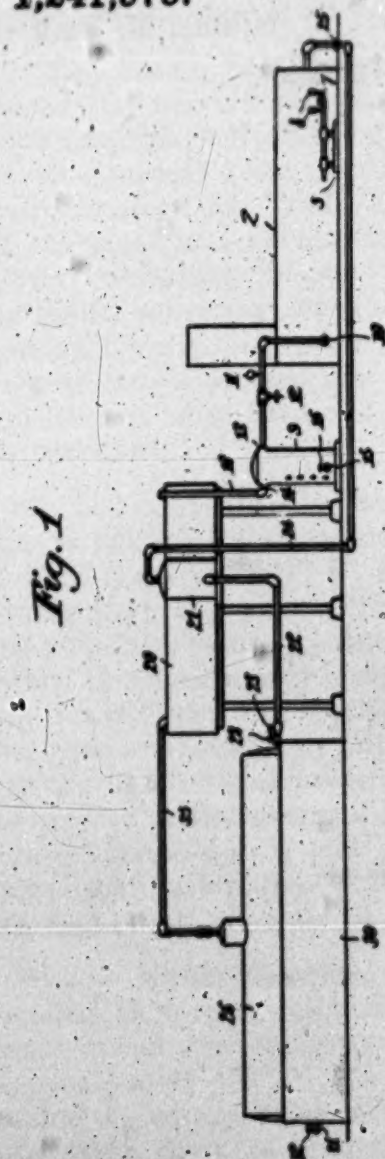


Fig. 1

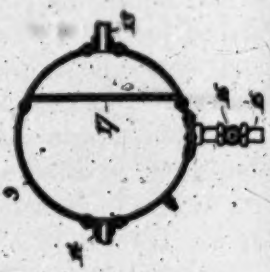


Fig. 4

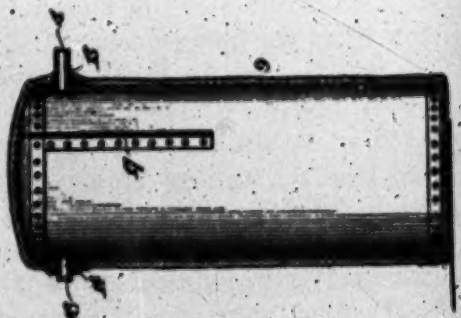


Fig. 3

Inventor,
Joseph E. Holmes.

Witnesses:
C. Reinke, Jr.
A. L. Hughes

By Victor J. Evans,
Attorney.

PX 228-1

[fol. 1372]

J. E. HOLMES.

PROCESS OF AND APPARATUS FOR PRODUCING LIGHT HYDROCARBONS.

APPLICATION FILED AUG. 31, 1915.

1,241,979. Patented Oct. 2, 1917.

2 SHEETS—SHEET 2.

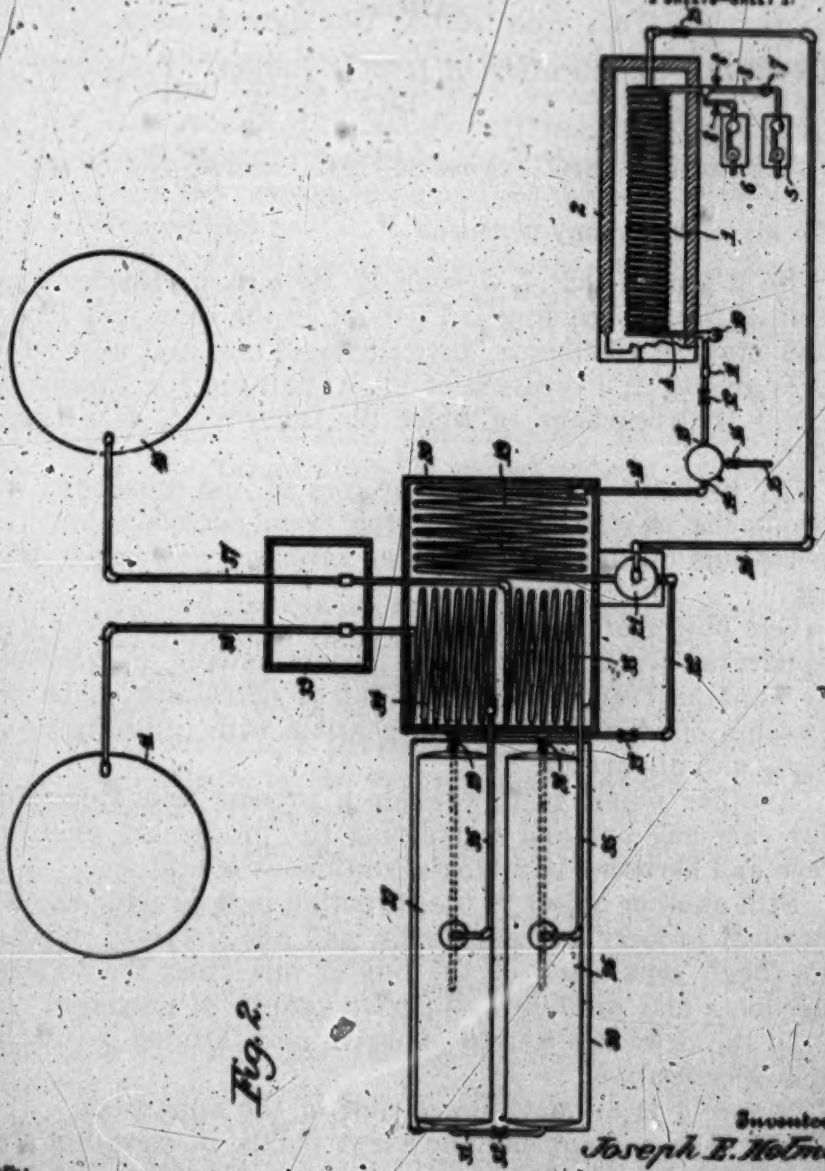


Fig. 2.

Inventor,
Joseph E. Holmes

Witnesses:
C. Deinle, Jr.
A. J. Hines

By Victor J. Evans
Attorney

304—378

[fol. 1373] United States Patent Office

Joseph E. Holmes, of Cushing, Oklahoma

Process of and Apparatus for Producing Light Hydrocarbons

1,241,979. Specification of Letters Patent. Patented Oct. 2, 1917.

Application filed August 31, 1915. Serial No. 48,318

To all whom it may concern:

Be it known that I, Joseph E. Holmes, a citizen of the United States, residing at Cushing, in the county of Payne and State of Oklahoma, have invented new and useful Improvements in Processes of an Apparatus for Producing Light Hydrocarbons, of which the following is a specification.

My invention relates to a process of and apparatus for producing gasolene and naphtha from petroleum oil and petroleum oil distillates, such as kerosene, gas oil and wax oil.

One object of the invention is to provide a method and apparatus which will yield a larger amount of gasolene or naphtha from a given amount of petroleum oil or petroleum oil distillate than is possible with ordinary processes and apparatus.

Another object is to provide a process and apparatus for carrying out and completing the production of gasolene and kerosene in a single continuous operation.

Still another object of the invention is to provide an economical process and apparatus, and one that will effect a thorough separation of the lighter oils from the heavier products and produce a superior quality of kerosene.

In the drawings hereto annexed, and forming a part of this specification,

Figure 1 is an elevational view of the apparatus.

Fig. 2 is a diagrammatic view, partly in elevation and partly in section, of the same.

Fig. 3 is a vertical section through the expansion drum.

Fig. 4 is a sectional plan view of the same.

In the practical carrying out of the present invention, I provide a primary retort or heater 1, heated from a suit-

able furnace 2, and embodying a coil of pipe of suitable length and diameter. Connected with the terminals of this coil are conducting pipes 3 and 4. The intake pipe 3 serves as a combined conducting and mixing conduit, in which the petroleum oil or petroleum oil distillate employed is commingled with natural gas, the oil and gas being forced through the pipe 3 to the coil 1 by means of suitable pumps 5 and 6, a meter 7 being provided in the intake pipe for indicating the amount of the oil pumped to the coil, and suitable gages 8 being arranged in the branches of said pipe leading from the respective pumps for indicating the pressures of the oil and gas.

The mixture of oil and gas forced into the coil 1, in the ratio of two volumes of gas to one volume of oil, is subjected therein, while under comparatively high pressure, to a comparatively high temperature, all the lighter volatiles being thereby vaporized in the coil and placed under high tension and pressure. In practice, the pressure in the retort 1 is varied from 50 to 100 pounds per square inch depending on the temperature, which is maintained at from 750 to 1100 degrees Fahr., depending on the density of the oil to be cracked.

From the coil the vapors and gas discharge through the outlet pipe 4 and pass to an expansion and separator drum 9, a pyrometer 10 and a gage 11 being provided in the pipe 4 to indicate the temperature and pressure, while also in said pipe is provided a pressure regulator 12, by means of which the pressure of the vapor and gas flowing to the expansion drum may be governed and the pressure and tension of the vapor and gas within the drum regulated to any desired degree.

The drum 9 comprises a cylindrical vessel having at its top an inlet 13 with which the pipe 4 is connected, and an outlet 14, and having at its bottom a drain pipe 15 having a controlling valve 16 therein, which pipe may form part of a pumping line, for forcing the heavier products into any suitable receiver. The inlet 13 and outlet 14 are separated by a vertically disposed baffle 17, whereby the vapor and gas entering the expansion drum are caused to pass downwardly into said drum and are prevented from taking a direct outlet through the outlet or discharge connection. The vapor and gases passing into the drum are thereby caused to expand under adiabatic conditions and

are thereby relieved of compression, thus allowing the heavier constituents to condense and precipitating the tar, coke and other heavier products which may be discharged through the pipe 16, while the lighter and more volatile constituents and gas remain in a vaporous and gaseous state, owing to their high temperature, and discharge through the outlet 14.

As stated, the pressure in the retort 1 may vary from 50 to 100 pounds per square inch and the temperature from [fol. 1374]750 degrees to 1100 degrees Fahr., dependent upon the density of the oil to be cracked. The temperature and pressure maintained by direct heat will at all times be such, with relation to the specific gravity of the oil under treatment, as to effect a thorough continuation of the vaporizable portions of the oil with the gas, and such also as to place the mixture in such conditions that when raised to a higher temperature and pressure, it will be adapted for adiabatic expansion to precipitate all of the heavy constituents. This higher temperature and pressure is secured by the use of the pressure regulator 12, which confines the mixtures in the retort, by establishing a resistance to its discharge, whereby the mixture is kept confined until heated to a degree higher than that required for the intimated mixture of its components. As a result the pressure of the mixture will also be raised until its temperature and pressure reach the proper stages to place the mixture in condition for adiabatic expansion, at which time the pressure of the mixture will be sufficient to overcome the resistance of the regulator 12 and the mixture will discharge from the retort and enter and expand adiabatically within the expansion drum.

The vapors and gas discharge through the outlet 14 pass through a pipe 18 to a primary condensing coil 19 arranged within a suitably cooled condensing box or chamber 20, in which coil the vapors are condensed, as will be readily understood. From the coil 19 the condensate and gas pass into a separator 21, in which the noncondensible gas is separated from the condensate, the condensate discharging through a pipe 22 containing a controlling valve 23, while the gas discharges through a pipe 24 having a controlling valve 25, through which pipe the gas may be conducted to any suitable point. In the present instance, the pipe 24 is shown as leading back to the retort furnace 2 for the pur-

pose of utilizing the gas as a fuel agent for heating purposes.

The pipe 22 leads to a pair of secondary stills 26 and 27 and is provided with valves 28 and 29 for controlling the flow of the condensate to the respective stills. As shown, the stills 26 and 27 may be arranged within and heated from a common furnace 30, which may be of any preferred type, and the stills may be provided with a common drain pipe 31 having a draw-off valve or cock 32, whereby the heavier particles or any residue remaining therein after distillation may be discharged and provision made for cleaning out the stills whenever required. Arranged within the condenser box or casing 20 are secondary condensers 33 and 34, the condenser 33 being connected with the still 26 through a valved vapor conducting pipe 35, while the still 27 is connected with the condenser 34 through a valved conducting pipe 36, in which condensers the gasolene and kerosene vapors will be respectively condensed. The gasolene and kerosene vapors thus condensed in the coils 33 and 34, may be discharged through discharge pipes 37 and 38 to a receiving house or point 39 and thence into tanks or other receptacles 40 and 41 in which the finished gasolene and kerosene are stored. It will, of course, be understood that the condensate from the separator 21 may first be distilled in the still 26, and the gasolene condensed in the condenser 33, and that the residuum from the still 26 may then be conducted into the still 27 to distil off the kerosene, which may be condensed in the condenser 34.

It will be seen that my improved process provides for the commingling with the oil or distillate under treatment of natural gas which contains a proportion of gasolene capable of being liberated under adiabatic compression, and that by the use of this gas the mixture when heated will be vaporized under high tension and pressure. As a result, the molecules of matter composing the oil are more thoroughly broken, thus changing their atomic weights and by reason of the great expansion of the mixture more efficiently separating the fine solid carbonaceous matter, with a result that there is a greater separation of the molecules forming the lighter hydrocarbons, such as naphtha, gasolene and kerosene, resulting in a much greater yield of the substances. Furthermore, by separating these liquids by adiabatic pressure, a more complete separation

of the lighter hydrocarbons from the heavier products will be affected. It will, of course, be understood that in this process all of the condensate from the separator may be conducted to both secondary stills and the gasolene and kerosene vapors separated and successively distilled off and condensed, and that after the oil has been once treated, if it should be desired not to make any kerosene, the remaining oil after the gasolene has been primarily taken off can be repeatedly put through the process until nothing remains but tar and gasolene. In this process a peculiar cracking of the oil is effected, as set forth owing to the great expansibility of the gas when heated and the capability of the petroleum oil to absorb gas when mixed therewith and introduced and treated in the retort 1 under high pressure and temperature. The gas, by reason of its expansibility, keeps the retort 1 full at all times and keeps the oil moving to the surfaces of the coil pipe. Under such conditions in the retort 1 no opportunity is afforded for the tar and sand to stop and adhere to the pipe, which would cause the oil to scorch and burn and leave an objectionable odor with the oil after passing through the retort. One objection to cracked oils is their disagreeable [fol. 1375] odor and the obstruction to the retort when the sediment and tar are allowed to stick to the retort, and burn into a hard scale or cake. By treating the oil in the presence of gas I eliminate the bad odor and increase the life of the retort in an obvious manner.

I claim:

1. An apparatus for producing gasolene or other like light hydrocarbons from a petroleum oil or distillate comprising a retort, means for supplying measured quantities of a petroleum oil or distillate and natural gas to said retort, means for heating the retort to raise the temperature and pressure of the mixture to a high degree, an expansion chamber in communication with the retort for the expansion of the mixture therein so as to condense and precipitate the heavier constituents, mean in the line of communication between the retort and expansion chamber for maintaining a predetermined pressure in the retort, and permitting flow of the mixture to the expansion chamber when such pressure is exceeded, and means for separating the

gas and heavy products from the lighter volatiles and condensing and collecting the latter.

2. The hereindescribed process of producing gasolene or other like light volatile hydrocarbon from petroleum oil or distillates, which consists in distilling a mixture of the oil or distillate with natural gas under a hgh temperature, whereby to raise the temperature and pressure of the mixture, causing expansion of the mixture under adiabatic conditions, separating the heavier from the lighter and more volatile constituents, and then condensing and separating the vapors.

3. An apparatus for use in producing gasolene or like light hydrocarbons from a petroleum oil or distillate comprising a retort, means for supplying a mixture of a petroleum oil or distillate with a predetermined quantity of natural gas to said retort, whereby to vaporize the oil and place the mixture under high temperature and pressure, means for causing expansion of the mixture under adiabatic conditions, and means for condensing and separating the vapors.

In testimony whereof I affix my signature in presence of two witnesses.

Joseph E. Holmes.

Witnesses: W. C. Rice, J. M. Rice.

[fol. 1376] PETITIONER'S EXHIBIT No. 229.

Complete Specification

Improved Process of and Apparatus for Distilling and Cracking Heavy and Light Hydrocarbon Residues

(Pages 2-5)

I, Albrecht Friedrich Georg Carl Paul Josef von Groeling, Engineer, of 55, Untere Viaduktgasse, Vienna, III, Austria, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

The present invention is for an improved process of and apparatus for distilling and cracking heavy and light hydrocarbons, and has for its object to provide for more efficient distillation and cracking of the hydrocarbons, and separation of the heavier hydrocarbons from those of lighter specific gravity, than has heretofore been possible.

In distilling hydrocarbons, it has already been proposed to vapourise heavy hydrocarbons and to heat such vapours in metal tubes to crack them or break them up before condensation.

It has also been proposed to vapourise heavy hydrocarbons in a still and to heat the vapours produced, and then subsequently, and in a portion of the apparatus other than that in which the vapours are thus heated, to intermingle the vapours with liquid hydrocarbons from a source other than the still, the liquid hydrocarbons being thus initially warmed and being subsequently fed to the still.

To effect an intermingling of the liquid hydrocarbons and the hydrocarbon vapours is advantageous and this step is adopted in the process according to the present invention. Additional advantages are secured, however, by arranging that the intermingling shall take place in externally heated cracking tubes, and this is the primary feature of the present invention.

Conveniently the liquid hydrocarbons, after the still vapours have been passed through them, are fed to the still, so that they will be initially warmed before they reach the still.

In one form of apparatus for carrying out this process the intermingling of the liquid hydrocarbons and the still [fol. 1377] vapours is effected by passing them in opposite directions through cracking tubes having means (such as worms) for impeding the progress of the fluids through the tubes and for causing a positive mixing of the fluids. According to another feature of the invention the intermingling of the liquid hydrocarbons and the still vapours is effected in cracking tubes which are heated externally by the furnace gases which also heat the still.

Other features of the invention are hereinafter pointed out.

For a more complete understanding of the invention reference is directed to the accompanying drawings, wherein

there is shown, by way of example only, one form of apparatus according to the invention.

In these drawings—

Figure 1 is an elevation, partly in section, showing the general arrangement of the apparatus; and

Figure 2 is a side elevation, also partly in section, of a part of the apparatus.

Like letters of reference refer to like parts in the drawings.

The apparatus comprises a still A mounted above a furnace B. The still is fed through the pipe C with hydrocarbons to be distilled and treated, and a pipe D with a branch D^1 at the bottom thereof supplies steam to the still. This steam is drawn from a super-heater E and the pipe E^1 connecting the super-heater to the pipe D is controlled by a suitable valve E^2. Situated adjacent the still is a series of cracking tubes F, shown in detail in Figure 2, these tubes being connected together at alternate ends by branches F^1 and heated externally.

By reference to Figure 1 it will be seen that the tubes F are arranged on the slant transversely. They may also be slanted longitudinally, alternate tubes slanting in opposite directions, for a purpose that will be indicated hereinafter. The lowest tube F is connected to the still by a pipe G which leads from a dome A^1 over the still. The highest tube F is connected by a pipe H to the bottom of a dephlegmator J. The highest tube F is moreover connected to the supply of hydrocarbons to be treated by a pipe K controlled by a valve K^1 and preferably connected to the tank containing the supply of hydrocarbons by a flexible connection K^2.

The tubes F are shown as situated in flues L, through which the furnace gases from the grate B pass after they have heated the still A. Suitable baffles may be arranged [fol. 1378] in these flues L in order to ensure that the furnace gases shall pass longitudinally from end to end over the tubes F.

Conveniently worms M are provided in the tubes F and if desired said worms may be rotated during the working of the apparatus. This, however, is not essential. The tubes F are so arranged that the worms M can readily be removed, either for cleaning or to allow the rate of flow of the liquids and vapours through the tubes F, to be regu-

lated. For allowing this easy removal of the worm M the ends of each tube F are closed by caps N which are secured in position by bolts. By merely unscrewing a set of these bolts a cap N can be removed and thus uncover a free aperture through which a worm can be withdrawn. In order to secure a tight joint at the ends of the tubes F, the latter are provided with flanged rings N^1 which, as will be seen from Figure 2, are grooved in order to receive annular projections on the caps N. Mounted on rings N^1 are other rings N^2 through which pass the bolts aforesaid. The construction just described provides a simple but effective, and readily removable closure to the ends of the tubes F.

The dephlegmator J which may be of any convenient type preferably comprises a series of internal pans situated one over another and so constructed as to collect sediment but allow the liquid to drip or flow down over them.

The dephlegmator J shown in the drawings is provided with three discharge connections for the liquid, i. e., the pipes O, P and Q. These discharge connections communicate with pans situated at different heights in the dephlegmator and permit of liquids of different specific gravity being drawn off. This method of withdrawing hydrocarbons of different densities is not claimed broadly in the present specification.

The pipe O, which is controlled by a valve O^1, can, by itself if necessary, completely empty the dephlegmator. The pipe P which is controlled by a valve P^1, can only empty approximately the top half of the dephlegmator, while the pipe Q, which is controlled by a valve Q^1, can only empty the extreme top portion of the dephlegmator. The pipes P and Q each comprise a U-branch P^2, Q^2 respectively.

Any permanent gas that may be evolved during the process may be collected from the top of the dephlegmator through the pipe R which is controlled by the valve R^1.

The operation of the apparatus is as follows: The hydrocarbons to be treated are fed in through the pipes K and K^2 to the upper tube F, and they find their way through the series of tubes F and the pipe C to the still A. Herein [fol. 1379] they are heated by the furnace gases, and steam from the pipes D and D^1 is bubbled through them. The mixed vapours thus obtained are collected in the dome A^1 and pass through the pipe G to the lowest of the cracking

tubes F. These tubes are externally heated, and owing to the worms M in the tubes, the vapours have to travel through a very long path and have a very long contact with the worms and the walls of the tubes before they can reach the pipe H and pass through to the dephlegmator.

The oil enters the highest tube F under a certain amount of pressure, which may conveniently be obtained by having the supply tank for the hydrocarbons arranged at some considerable height above the tubes F. The pressure at which the hydrocarbons enter the tubes F can be regulated by adjusting the height of the supply tank, this being possible by reason of the employment of the flexible connection K^2. By reason of the fact that the liquid hydrocarbons enter the tubes F under a certain amount of pressure they will travel round the worms M, intermingling with the vapours from the still which are also travelling around the worms M, and thus will be initially warmed before they reach the still A. Moreover, the vapours themselves will be scrubbed and purified, and sediment contained in them being abstracted by the liquid hydrocarbons through the tubes F may be facilitated by slanting the latter transversely and longitudinally in the manner described above.

The vapours which pass off through the pipe H from the tubes F, enter the dephlegmator near its bottom and then pass upwards through the latter by a long and tortuous path. During the passage of the vapours through the dephlegmator they condense, the hydrocarbons of the greatest specific gravity coming down first, naturally, and these can only be drawn off through the pipe O. Vapours of hydrocarbons of a moderate specific gravity can be withdrawn through the pipe P, while the lightest hydrocarbons will be drawn off through the pipe Q. As already described any permanent gas which may be generated is withdrawn through the pipe R. The temperature adopted is so chosen that very little, if any, permanent gas is evolved. The temperature, however, may be much higher at one time, where the oil being treated is "difficult", while at another time the temperature may be considerably lower, with a different class of oil. The temperature is also influenced to a certain extent by the pressure under which [fol. 1380] the treatment is effected; usually, however, the temperature will range between 350 and 500° C., in the still and cracking tubes. These figures, of course, are only

given by way of example and they do not by any means determine the limits of temperature which may be adopted. For instance a heavy oil may require a temperature in the still gradually rising from 280° C. to 400° C., while the temperature in the cracking tubes would require to be less than the temperature in the still to prevent the cracking of certain impurities contained in the oil.

The pressure of the gas or hydrocarbon vapours is usually approximately 1 to 1.5 atmospheres, this pressure being set up by the obstacles placed in the path of the vapours from the still to the draw-off cocks from the dephlegmator. The pans in the dephlegmator exert a considerable baffling effect on the vapours. The pressure of the liquid hydrocarbons is usually only sufficient to cause the flow of the liquid through the cracking tubes to the still. It is produced by the height of the feeding tanks from which the pipe K^2 leads and may be altered by varying the height of the tank.

Usually all or substantially all the cracking of the vapours will take place in the tubes F, but possibly in some cases some cracking may occur at the upper part of the still A.

It will of course be understood that it is not essential to heat the tubes F by the same furnace gases as which heat the still. On the contrary the tubes F can, if desired, be provided with a separate flue and furnace for direct heating. By this means the temperature of the tubes may be regulated independently of that of the still, should this be desirable in the course of the process. The process can be continuous, two or more stills being suitably arranged to allow of one or more of them being worked while the other or others are being charged with residues, preparatory to being brought into operation when the treatment in the former stills has reached a certain point.

It will be seen that the present invention provides for the conversion of heavy hydrocarbons into lighter hydrocarbons and for the separation of the heavy hydrocarbons from those of lighter specific gravity. Light oils, such as petrol, can be derived from heavy and viscous residues, while the latter can also be converted into suitable and marketable Diesel oils of very low viscosity.

The invention is of course not limited to the precise de-
[fol. 1381] tails hereinbefore set forth, but on the contrary

may be modified in many respects without departing from the spirit of the invention; for example the hydrocarbons may be supplied to the pipe K under pressure from a force pump.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. A process for distilling and cracking hydrocarbons, in which hydrocarbon vapours from a still are passed prior to condensation through externally heated cracking tubes (for example the cracking tubes F heated by the furnace gases which also heat the still Figure 1) in which they are intermingled with liquid hydrocarbons from another source, for the purpose described.

2. A process according to preceding Claiming-clause No. 1 in which the liquid hydrocarbons, after the still vapours have been passed through them, are fed to the still.

3. Apparatus for carrying out the process according to preceding Claiming-clause No. 1 or No. 2, wherein the intermingling of the liquid and vapours is effected by passing them in opposite directions through cracking tubes having means (for example the worms M) for impeding the progress of the fluids through the tubes and for causing a positive mixing of the fluids.

4. In apparatus for carrying out the process according to preceding Claiming-clause No. 1 and No 2, the employment of a series of heated tubes each tube having therein a worm (for example M) which may readily be removed from within the tube (for example by detaching the cap N from the tube) for the purpose of regulating the speed of flow of the hydrocarbons through the series of tubes.

5. The process and apparatus for distilling and cracking hydrocarbons, substantially as described or illustrated in the accompanying drawings.

Dated this 29th day of October, 1913.

Boult, Wade & Tennant, 111/112, Hatton Garden, London, E. C., Chartered Patent Agents.

Redbill: Printed for His Majesty's Stationery Office, by Love & Malcomsen, Ltd.—1914.

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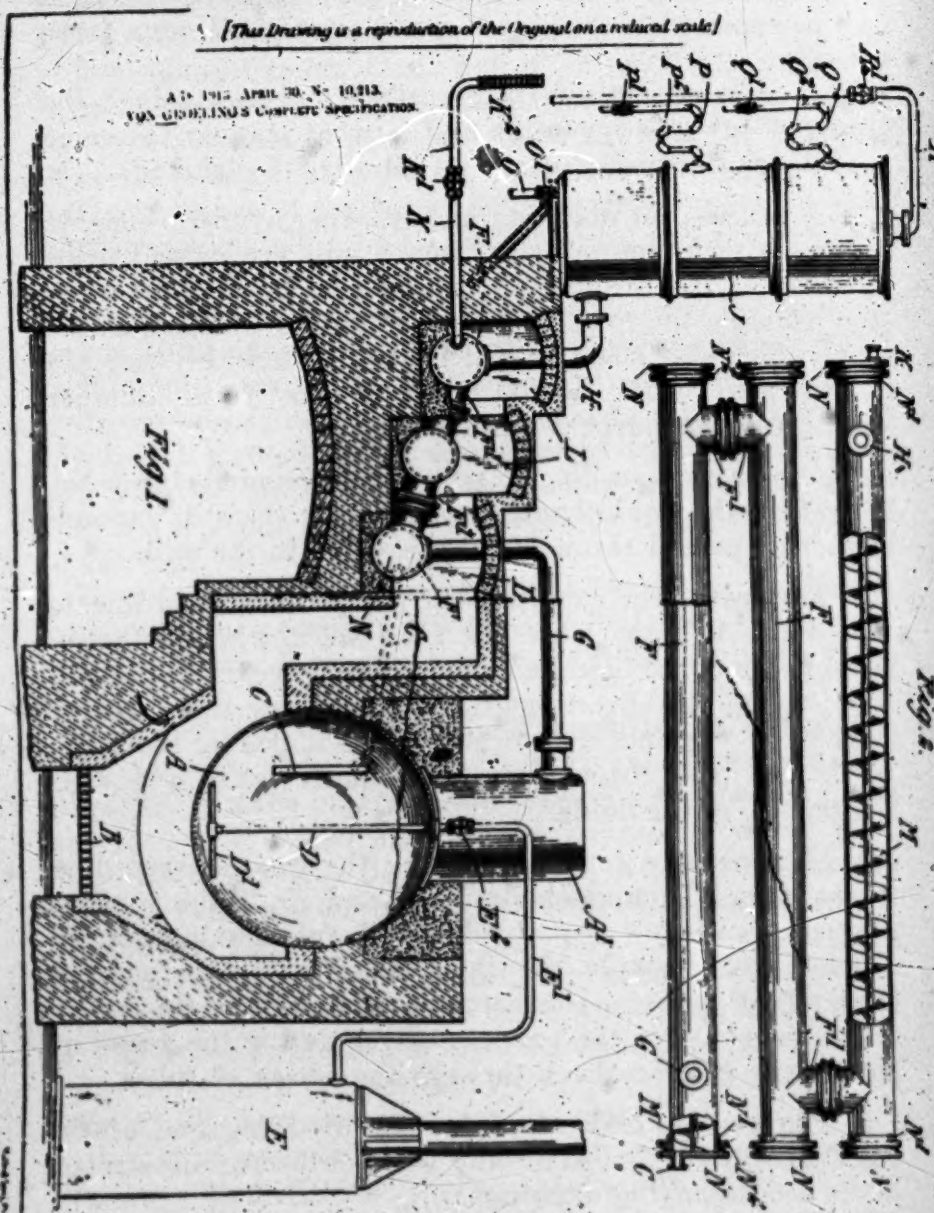
[fol. 1382]

[This Drawing is a reproduction of the Original on a reduced scale]

A.D. 1913 APRIL 30. N° 10,313.
VON GIESELING'S COMPLETE SPECIFICATION.



[fol. 1383] PETITIONER'S EXHIBIT No. 230

No. 23,446. (Coat of Arms.) A. D. 1911

(Filed U. S. Patent Office Aug. 19, 1912)

Date of Application: 24th Oct., 1911. Accepted: 11th July, 1912

Complete Specification

Improvements in Apparatus for the Destructive Distillation of Mineral Oils and the Like

(Pages 1-3)

I, John Laing, F.I.C., of 18, Links Place, Musselburgh, Chemist, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to apparatus for the treatment of mineral oils by destructive distillation to obtain lighter products, the distillation being conducted at or near atmospheric pressure or at higher pressure, according to the nature of the oil to be treated, and the products to be obtained.

In the Specification of my prior British Patent No. 4120 of 1890 I have described an apparatus for the treatment of mineral oils consisting of a still or boiler divided into compartments connected to corresponding condensers. In the use of the said apparatus it was found difficult to obtain a steady running distillate, on account of cold oil from the said condensers entering the still and thus bringing the oil therein below boiling point. Also, if the oil operated on was not free from water before distillation began, the further drawback was encountered that the water on being distilled re-condensed, and returning to the still—now at a higher temperature—flashed into steam and thus was very liable to prove dangerous in its effects.

In order to overcome these drawbacks, in accordance with the present invention, I interpose, between the said condensers and the still, traps or collectors equipped with

suitable devices for permitting discharge of water therefrom and provide means for leading the condensed oil through the oil contained in the still, the arrangement being [fol. 1384] such that the oil vapour condenser by each of the said condensers collects within its corresponding trap, then overflows and is conducted through the heated oil in the still in such manner that said condensed oil is heated in its passage and is discharged within the still at a point above the level of the oil contained therein; the temperature being such that the continuous distillation proceeding in the still is not disturbed to any appreciable extent.

It will thus be seen that by the adoption of devices such as above described I avoid the trouble caused by the presence of water in the oil and ensure that the oil shall be in a heated condition before its return to the still.

Other features of the invention will appear from the following description.

The figure of the accompanying drawing is a part elevation, part longitudinal vertical section showing diagrammatically a preferred construction of apparatus embodying the invention.

Referring to the drawing, the apparatus comprises, as heretofore, a still or boiler A which is divided internally into compartments, such as indicated at B, C, D and E, by means of vertical partitions F, which do not reach the bottom of the still, and a series of condensers G, connected to the still by means of pipes G^1, the oil to be operated on being delivered by means of a pipe H, each of the compartments following the compartment connected to the pipe H receiving oil from its corresponding condenser G; the said condensers may be located in any suitable position and may be supported in any suitable manner.

Interposed between each condenser G and the still is a trap or collecter I provided with a cock $I^{\times}$ for permitting discharge of water therefrom, and with a gauge glass, the condensed oil passing by way of a pipe K connected adjacent to the upper end of the trap, and being led thence into the still and through the liquid therein, the lower end of the said pipe being desirably of sinuous shape, and the outlet K^1 thereof being disposed above the level of the liquid in the still; the traps or collectors I may be located in any suitable position and may be supported in any suitable manner.

If desired, oil may be employed in lieu of water for condensing purposes, the oil to be fed to the still being caused [fol. 1385] to pass through the condenser jackets and being heated by the oil vapour passing through the coils of the condensers, the heated overflow oil passing to the still. In this way a great economy of fuel may be effected.

The further treatment of oil distilled in the still A is now effected in apparatus substantially such as described in the Specification of Letters Patent No. 11,757 of 1890.

The vapours evolved in the still A pass off through a pipe N by way of a valve e. g., a valve R, adapted to be loaded by means of a weighted lever S acting on the valve spindle and thence through a branch pipe T to a relief tank V where they are reduced as nearly as possible to atmospheric pressure, what is condensed in the tank being run off by the syphon pipe Y, and the uncondensed vapours passing by way of pipe X to a pipe O and so to a worm P; or, instead of being led through the branch pipe T, the vapours may be led directly from the pipe N to the pipe O and thence to the condensing worm P, the valve R being relieved.

The stop valve Q and syphon pipe Z correspond to the stop valve and syphon pipe indicated as E and Z respectively in the drawing annexed to the Specification of Letters Patent No. 11,757 of 1890.

A suitable connection, e. g., a T-piece fitted with stop cocks may be provided to lead any uncondensed gases from the condensing worm P back to be absorbed by the vapours leaving the still at the first compartment of the still, or the relief tank V or the pipe O.

The still A may be suitably inclined so that the heavy residues or pitch may be readily run off as desired. By this means distillates may be obtained of very low specific gravity suitable for motor car spirit, or for any other purpose for which light mineral spirit or oils may be found useful.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:

(1) In apparatus for the destructive distillation of mineral oils and the like comprising a still divided into com-

partments, tubular connections for leading vapour and oil from compartment to compartment, and condensers fitted in said connections: the provision of a receptacle affording a water trap interposed between each condenser and its succeeding compartment, as and for the purpose specified.

(2) Apparatus of the character indicated in the preced- [fol. 1386] ing claim wherein from each water-trap receptacle there is led a pipe connection including a preferably sinuous part which is immersed in the liquid in the still, and the free end of which extends above the level of the liquid in the still, substantially as and for the purpose specified.

(3 Apparatus for the destructive distillation of mineral oils and the like as above claimed, provided with connections for leading back uncondensed gases to be reabsorbed by the vapours coming from the still, as hereindescribed.

Dated this 24th day of October, 1911.

Cruikshank & Fairweather, Limited. Harold Cruikshank Fairweather, Director, International Patent Agency, 65-66, Chancery Lane, London, W.C., and 62, Saint Vincent Street, Glasgow, Agents for the Applicant.

Redhill: Printed for His Majesty's Stationery Office by Love & Malcomson, Ltd.—1912.

[fol. 1387]

A.D. 1911 (No. 21 N° 25414.
LAING'S (Gerard Electrolyser)

[This Drawing is a reproduction of the Original on a reduced scale.]

[fol. 1388] PETITIONER'S EXHIBIT No. 231.

No. 3413. (Coat of Arms.) A. D. 1913

Date of Application: 10th Feb., 1913. Accepted: 19th Feb., 1914

Complete Specification

Process and Apparatus for the Transformation of Petroleum and Similar Hydrocarbons into Products Having a Lower Boiling Point

(Pages 1-3)

I, Georges Renard, of 125, rue de Trone, in the City of Brussels, Belgium, Gentlemen, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to a process and apparatus for transforming petroleum and similar hydrocarbons into products of lower boiling point by the application of heat and pressure. In this connection it has been proposed to force the hydrocarbon under pressure through heated piping in which its temperature is raised above boiling point, the heated liquid being then allowed to escape and vaporise in a heated chamber from which it is led away and condensed.

According to the present invention the petroleum or similar hydrocarbon is forced as a liquid stream through an uninterrupted passage the first part of which is maintained at a temperature above boiling point and the remainder serves for cooling purposes, the pressure maintained throughout the travel of the fluid being in excess of its vapour tension.

In carrying out the process I preferably adopt a temperature of from 400° to 450° C and a pressure of 40 to 50 atmospheres; these conditions give rise to the formation of new atomic groupings and novel products with a lower boiling point than the petroleum or other hydrocarbon subjected to the treatment.

A convenient form of apparatus for carrying the process into effect embodies a continuous length of tubing the first

part of which is heated to serve as a super-heater and the remainder cooled to serve as a cooling device, means being [fol. 1389] provided at one end for forcing the liquid through the tubing and means at the other end for offering resistance to the free passage of the liquid and thereby maintaining a pressure upon the liquid.

The superheater part of the tubing may be immersed in a molten lead bath whilst the cooling part is immersed in a water bath, the two parts being uninterruptedly connected but situated at a convenient distance from one another.

In order that the invention may be clearly understood and readily carried into effect I will now proceed to describe the same more fully with reference to the accompanying drawing which shews diagrammatically a suitable apparatus used in carrying out the process.

1 designates the superheating part and 2 the cooling part of a single length of high pressure steel tubing, the two parts being arranged in series and forming a continuous uninterrupted watertight conduit.

At the inlet end of the tubing a pump A is arranged; there is also provided a non-return valve B, an air chamber C, and a pressure gauge D; the pump serves as a means for introducing the liquid petroleum or similar hydrocarbons into the tubing. The superheating part 1 is placed in a molten lead bath E which maintains the required heat, which is evenly distributed through the length of this part. The cooling part 2 is immersed in a water bath F. and serves to cool the liquid that has been subjected to superheating in the part 1.

The outlet end of the tubing is provided with a pressure governor G which permits of maintaining the required pressure throughout the tubing. This pressure is suitably regulated to be superior to the tension of the vapours at the temperature of the superheating part 1 so that there cannot be any vaporisation of the liquid under treatment whereby the latter traverses the whole of the length of the tubing in a liquid state.

The superheating part 1 is of great length proportionately to its diameter so that the liquid traversing the same will be subjected to the action of heat for a long time, the speed of travel also being determined to that end.

In using the apparatus the pump A is started and fed with the liquid. The pressure governor G provided at the

outlet end of the cooling part 2 is slightly opened so as to [fol. 1390] permit the escape of air and the filling of the whole length of tubing with liquid. This having been done, the governor G is then so regulated that the pressure gauge D indicates about 40 atmospheres; it is under this pressure and at a heat of about 400—450° C that the liquid hydrocarbon is made to progress through the tubing. The issuing cooled hydrocarbon is collected at the outlet end of the part 2. The petroleum has formed new atomic groupings owing to the influence of the conditions obtaining in the tubing.

By subsequent distillation the product can be separated into substances having different densities.

The apparatus acts in a manner somewhat similar to a sealed tube used in chemical laboratories but the duration of the application of the heat is determined by the speed of travel of the liquid or the length of the superheating part 1 of the tubing; this length may attain three hundred metres in commercial applications.

From another point of view the apparatus constitutes a kind of Papin's digester with continuous action adapted to work at an exceedingly high pressure without the least danger of explosion.

A distinctive feature of the apparatus is that it possesses a considerable heating surface as compared with the small volume of liquid travelling in the tubing. This surface is, in fact, 1 square metre for every 1177 cubic centimetres of liquid.

It may be mentioned that a length of tubing that has been found satisfactory was composed of nickel steel and measured 10 mm. inside diameter, 21 mm. outside diameter, and 60 metres long.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. A process for transforming petroleum and similar hydrocarbons into products of lower boiling point, consisting in forcing the petroleum or the like as a liquid stream through an uninterrupted passage the first part of which is maintained at a temperature above boiling point and the remainder serves for cooling purposes, the pressure maintained throughout the travel of the fluid being in excess of its vapour tension.

2. A process for transforming petroleum and similar hydrocarbons into products of lower boiling point, by forc- [fol. 1391] ing the petroleum or the like through an uninterrupted passage, in which the first part of the passage is maintained at a temperature of about 400—450°, and the pressure maintained throughout the passage is from forty to fifty atmospheres.

3. Apparatus for transforming petroleum and similar hydrocarbons into products of lower boiling point, comprising a continuous length of tubing the first part of which is heated to serve as a superheater and the remainder cooled to serve as a cooling device, means for forcing a stream of the liquid to be treated through the tubing, and means at the outlet end of the tubing for offering resistance to the free passage of the liquid, for the purposes specified.

4. The method of and apparatus for transforming petroleum and similar hydrocarbons into a product of lower boiling point, substantially as described.

Dated this 10th day of February, 1913.

Haseltine, Lake & Co., 28, Southampton Buildings, London, England, and 60, Wall Street, New York City. U. S. A., Agents for the Applicant.

Redhill: Printed for His Majesty's Stationery Office by Love & Malcomson Ltd.—1914.

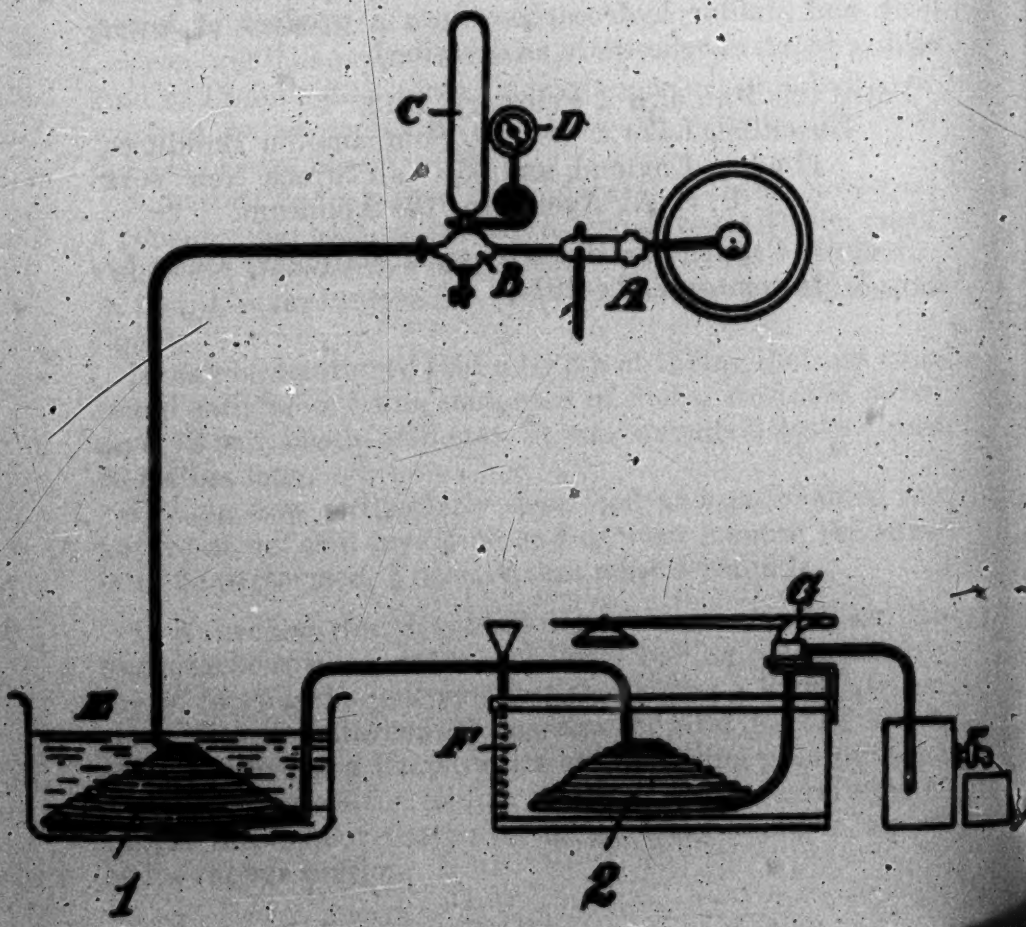
4872

[fol. 1392]

A.D. 1913. Feb. 10. N° 3413.

RENARD'S Complete Specification.

(1 Sheet)



[fol. 1393] PETITIONER'S EXHIBIT No. 232

A Practical Treatise on Petroleum, Comprising Its Origin, Geology, Geographical Distribution, History, Chemistry, Mining, Technology, Uses and Transportation, Together with a Description of Gas Wells, the Application of Gas as Fuel, etc., by Benjamin J. Crew, with an appendix on the Product and Exhaustion of the Oil Regions and the Geology of Natural Gas in Pennsylvania and New York

By Charles A. Ashburner, M.S., C.E., Geologist in Charge, Pennsylvania Survey, Philadelphia

Illustrated by Seventy Engravings and Two Plates

Philadelphia: Henry Carey Baird & Co., Industrial Publishers, Booksellers, and Importers, 810 Walnut Street.
London: Sampson Low, Marston, Searle & Rivington, Crown Buildings, 188 Fleet Street.

1887

(Pages 280-285, 288-291)

The Distillation and Utilization of Residuum

After all the oil that can be safely run into the illuminating oil has been removed from the still, and when the darkened product would impair or imperil the color-test, the fires are usually withdrawn from the still and preparations made to remove the residuum and the coke. Some refiners prefer to continue the distillation a short time longer to recover a small percentage of oil, dark though it may be, which is run over with a fresh portion of crude oil. Where the crude oil is of light gravity this proceeding is unobjectionable and may be profiable; but when the crude oil is of heavy gravity, the propriety is questionable, [fol. 1394] and its profitableness exceedingly doubtful. In former years it was customary to allow the still to cool for several hours after the fire had been withdrawn. The residuum was withdrawn through a tail pipe at the rear of the still. This could not be done immediately after the fire was withdrawn, as at the high temperature of the con-

tents of the still at the completion of the process of distillation, the residuum would instantly take fire upon exposure to the oxygen of the atmosphere. Several dangerous fires resulted from this early mode of procedure. The residuum is now withdrawn by means of a pipe connected with a steam pump. The pipe passes by several returns of the same through a tank of cold water, which cools the residuum sufficiently to obviate this danger. It is pumped into a large settling reservoir or tank, where it is allowed to stand for several days to allow of the subsidence of all the fine particles of coke, which will separate by this process. This tank is provided with an exit pipe placed at the distance of about twelve inches from the bottom of the tank, to admit of the drawing-off to the clear liquid, while a large opening or man-hole is placed on the side at the bottom to admit of the removal of the sediment. This is in the condition of slush, and is exclusively employed as fuel for the stills or boiler by mixing the same with fine coal dust or coke screenings. The residuum thus purified is pumped into storage tanks. In this condition it is either sold to the manufacturer of paraffine-wax and lubricating oils, or for the manufacture of gas, for which it has been largely employed, either to enrich the gas product of coal, or by itself.

Treatment of Residuum

If there were any dividing line between the business of manufacturing illuminating oils and that of making lubricating oils, this would be a proper place to make it, but in practice it is impossible to place this line, as it would be difficult to find two refiners who confine themselves exclusively to the same class of products; while some of the largest manufacturers who formerly devoted themselves entirely to one grade even of illuminating oil, now find it both convenient and profitable to handle most, if not all, of the various products which can be made from the crude oil. We shall therefore pursue the method which we have adopted, of describing the different processes employed, [fol. 1395] assuming for convenience' sake that all are practised under one management.

After the subsidence of all the coke, the residuum is transferred by means of a pump to the residuum stills.

These are generally built on the cylinder pattern, and should not much exceed two hundred barrels' capacity, and are set in banks of three. In stills of larger capacity, it has been found in practice that the quantity of solid coke residue is so great that the heat necessary to drive the still to dryness is so intense as to severely strain the bottom, making frequent repairs necessary. The ordinary forms of condensers can be employed, excepting that the tanks containing the water are furnished with a steam pipe, in order that, in cold weather, the water may be warmed sufficiently to keep the dense paraffine oil passing through the pipe in a liquid condition; otherwise, the pipe may be so choked up with solid paraffine as to endanger the life of the operator from an explosion. In warm weather there is very little risk of this kind, but in extremely cold weather the distiller should be constantly on the alert to discover the first appearance of a stoppage from this cause. If, in weather of this description, the flow of oil is checked, with the ordinary fire under the still, the safest course will be to withdraw the fire, unless the condenser itself is supplied with a steam pipe by which a jet of live steam may be made to pass through the pipes and thus clean them.

In a number of paraffin-oil manufactories, air condensation is employed, and water tanks entirely dispensed with. The condensation is effected through cast- or wrought-iron pipes of eight or ten inches in diameter, suspended in the air; the pipe rising by a slow gradation as it passes from the still. This pipe is provided with outlets at certain intervals to admit of the removal of the heavier oils, which are the most rapidly and readily condensed. This is perhaps, a modification of the Atwood condenser.

When the still is loaded, and the fire started, the distillation commences. The first runnings from twenty to twenty-five per cent. (if the residuum be of good gravity), say of 20° to 21° B., will be found sufficiently light in gravity to be transferred to the crude oil tank and re-distilled from this. From that point down to the emptying of the still, paraffine oil constantly pours forth from the tail-pipe of the condenser, gradually deepening in color and increasing in density. If the paraffine oil is to be sold without further manipulation, the whole distillation is generally

[fol. 1396] run into one tank, leaving the further manipulation to the manufacturers of paraffine wax and lubricating oils. If the handling of the distillate is contemplated by the distiller of the residuum, another course is pursued, and we here merge our operations into the domains of the manufacture of lubricating oils and paraffine wax, which is in many places quite a distinct business. Here again is a subdivision of this multiform product. The manufacturer of wax selects his crude material from the various samples of heavy oil offered to him, being guided in his choice both by its gravity and color, and the percentage of wax it contains. The manufacturer of machinery or lubricating oils finds himself in a wilderness of oils of all kinds, animal, vegetable, and mineral, the peculiarity of all and each of which he is obliged to make himself acquainted with to adapt them by an infinite number of combinations and mixtures to suit the various tastes, whims, or actual experience of his customers.

Paraffine Wax and Its Manufacture

While paraffine in a fossil state under the names of earth-wax, or ozocerite, has been known in Europe from the earliest times, the modern discovery that it is a product of the distillation of several organic bodies under high temperatures, belongs fairly to the chemist Karl Reichenbach, who gave to the strange compound it- present name, from parum and affinis, because it appeared to him to be wholly destitute of chemical affinities. His discovery, and its peculiar behavior in this respect was published in the year 1830. The following year, its presence in the petroleum of Rangoon, was noticed by Christison, of Edinburgh. He called it petroline, but hearing subsequently of Reichenbach's discovery, he was satisfied of the identity of the two substances, and withdrew the name given by himself. In 1833, 1834, and 1835, we have records of the separate discoveries by the three chemists, Laurent, Gregory, and Viobel, the former showing that the oils distilled from shale contained paraffine.

From this time on organic chemistry was making rapid advances, and we have frequent allusions to its presence in a number of compounds as a result of destructive dis-

tillation. To no one person does the credit more properly belong of founding the commercial industry based upon the manufacture of paraffine and its allied products than to [fol. 1397] Seligue, of France. Largely to his genius and indefatigable industry belong the many improvements made in the manufacture of oil from bituminous shale. Did our space permit, we would be glad to reproduce here Professor F. H. Storer's remarks on the discoveries of Seligue in connection with the paraffine industry. We have room only for the following brief extract, which succinctly details the various products secured by him:

"On the 27th of March, 1839, Seligue specifies certain additions and improvements to a former patent. In alluding to the use of his oils in the treatment of cutaneous diseases, he speaks of the three large establishments for the distillation of bituminous shale, which he has erected in the department of Saône et Loire, and mentions the fact that the oil (crude) is furnished at the rate of ten centimes per pound. The clearest of all of Seligue's specifications, however, is that of the patent granted to him March 9, 1845, for the bituminous shales and sandstones. After describing the various forms of apparatus used in distilling, into one of which superheated steam was introduced, he enumerates the products of distillation as follows: I. A white, almost odorless, very limpid mineral oil, somewhat soluble in alcohol, which may be used as a solvent or for the purpose of illumination in suitable lamps. II. A sparingly-volatile mineral oil of specific gravity 0.84 to 0.87, of a light lemon-color, perfectly limpid, almost odorless, never becoming rancid, and susceptible of being

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methods employed there, anything which will aid us in our present work.

In treating this subject from the stand-point of the American refiner, the preparation of lubricating oils and the manufacture of paraffine wax run so closely together, that in some points at least they touch, and must be treated as though they belonged to one subject. The manufacture of either or both begins when the residuum is placed in the still. The first products of this distillation down to about

32° Baumé (which when they are received into one tank, constitute an oil of 38°), are returned as crude oil.

The Production of Illuminating Oils

After the separation of this first part, the products of the still are either again subdivided into at least two run- [fol. 1398] nings, or run into one tank, according to the peculiar views of the refiner and the wants of his customers. If received into one tank, the oil is pumped into the "paraffine agitator." This apparatus is constructed upon the same general principles as the agitator used for illuminating oil, excepting that it is provided with special arrangements for heating its contents and retaining the dense easily congealed oil in a liquid condition. This is readily accomplished by surrounding the agitator with a steam-jacket, which not only supplies the facilities for applying the heat when required, but also affords a protection to the sides of the tank from the chilling effects of the cold during the winter. In the absence of this, in very cold weather, it will be almost impossible to treat paraffine oil on account of the solidification of the paraffine upon the internal surface of the tank; no more heat should be employed than is actually necessary to maintain the contents in a fluid state, and the paraffine entirely melted. The same general principles of chemical treatment followed in the case of illuminating oil are observed here. The amount of acid used is much larger, and is regulated by the gravity and color of the distillate. Three, four, or even five per cent. in volume is employed. Its action upon the oil is very energetic, accompanied with the disengagement of an abundance of sulphurous acid vapor, and the subsidence of a heavy "acid sludge," requiring exit-pipes and stop-cocks for drawing it off, to be of larger diameter than those ordinarily employed. The "sludge" upon standing becomes quite solid, and is entirely a waste product. The treatment is following by the usual water- and alkali-washing. Care should be taken throughout, that the proper temperature be preserved, so that the paraffine shall be maintained in perfect solution. When this operation is completed, the oil is either allowed to flow by gravity, or it is pumped into tanks, provided with a steam

coil, in order that its contents may be preserved in a perfectly limpid condition to permit of the settling of the water. This being withdrawn through a stop-cock at the bottom of the tank, the contents are removed to another apartment, the temperature of which has been artificially lowered by a freezing machine, where it is subjected to the chilling process.

In the winter the ordinary temperature is sufficient to crystallize the paraffine. If the process is to be carried on during the warm weather, the contents of the tank are [fol. 1399] barrelled, and the temperature of such a room may be reduced by a good apparatus to 10° or 15° F., even in very hot weather. An exposure of the paraffine oil for forty-eight hours to this temperature chills the whole mass to a complete solid. From the packages, the contents are shovelled out into small cotton bags of very strong material and subjected to powerful pressure by means of a hydraulic press. This pressure is slowly applied and gradually increased, the operation being one requiring skill and experience. If the pressure be too rapid and too severe, especially at the commencement, a notable percentage of paraffine crystals will be forced through the interstices of the bagging, attended also probably with a rupture of the same, and a serious contamination of the oil that has already passed through. Unless this operation be skillfully conducted, enough crystallized paraffine, it may be in very fine particles, will pass through the bagging, to interfere materially with the "cold-test" of the oil. In the event of a difficulty of this kind, simple straining through coarse muslin will frequently remove these coarse particles of floating crystals. This operation must of course be done in an apartment where the temperature is sufficiently cold to prevent their melting.

We have now divided the product of the distillation of the residuum into three parts: 1st. The lighter oils, which have been returned to the crude oil tank. 2d. The crude paraffine, which for the present we leave in the presses; and 3d. The refined heavy oil, which in its present shape may be either sold for lubricating purposes, or subjected to further treatment for special purposes. The gravity of this should be about 32° B., and the fire-test 325°, and the cold-test 30° F.

Quite a high temperature is necessary to drive all the volatile portions of the residuum, and before the residue of this

is completely converted into coke, the bottom of the still becomes red-hot, and yellow vapors issue from the tail pipe; very near the close of the operation there distils over a dense, resinous, product of a light-yellow color, of a solid consistence in even moderate weather, and becoming quite brittle in cold weather. It readily sinks in water, having a specific gravity of about 1.25. It exhibits in a very high degree the iridescent properties of petroleum, to such extent indeed, that it has been supposed by some to be the peculiar compound which imparts to petroleum its rainbow hue. Pro- [fol. 1400] fessor Morton, of the Stevens Institute of Technology, who investigated its properties some years ago, obtained from it two bodies, exhibiting a high degree of fluorescence, for which he proposed the names, thallene and petrolucene. As it readily dissolves in paraffine oil, it has been added to these for the purpose of increasing their density for lubricating purposes.

For the present, we leave the further consideration of lubricating oils, and having obtained paraffine in a crude state, will take up the process of

Refining Paraffine Wax

From the refined paraffine oil, prepared and chilled as above described, there should be obtained about three-

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[fol. 1401] Translation of Petitioner's Exhibit No. 246

The Mineral Oil—and Paraffin—Factories of the A. Riebeck Monton Werke Company in Halle a/S., Dedicated to the Participants of the Fourth German General Mining Assembly at Halle a/S 1889

Halle a/S
Printed by the Printing Office of the Orphanage

P. 9

The Webau factory uses as starting material the tar of the saxonian brown coal and in particular it works up the tar of the distilleries at Webau, Runthal, Willschuetz,

Tackau, Gaumnitz (a total of 300 furnaces) as well as tar bought occasionally outside.

Webau can work up to 12000 double hundredweights of tar per month and takes beside the hard paraffin produced in Reussen also per year several thousands of double hundredweight of raw paraffin of other manufacturers for a further treatment.

For the working up of the brown coal tar principally four operations enter into consideration:

the distilling,
the treatment with chemicals (mixing process),
the crystallizing,
the de-oiling of the paraffin (pressing).

The brown coal tar contains carbon and hydrogen compounds (hydrocarbons of the methane series and the ethylene series, paraffines and olefines; hydrocarbons of the aromatic series have not been found up to the present), oxygen-containing hydrocarbons (acid bodies, resins), nitrogen-containing hydrocarbons (picolines) and sulphuretted hydrocarbons (mercaptaines and higher thiophenes).

In its distillation it is not only a question of the physical process of separation according to the boiling point, but there is also always carried out a chemical process, a decomposition, which it is the task of the distiller to keep within the proper limits. The "too little" must be avoided [fol. 1402] just as well as the "too much."—The entire saxo-thuringian industry works with distillation stills of cast iron, approximately the same capacity—about 2000-3000 kilograms of content.

The condensing worm is ordinarily of lead pipe and stands in a lead or iron cooling vat, the distillation takes place over the open fire.[1]

In the Webau factory the distillation since 1884 is carried out in a vacuum and method and apparatuses differ correspondingly from those of the rest of the industry. The vacuum distillation had already shown its advantages in the manufacture of stearin, in the distillation of glycerine and in the distillation of coal tar. The essential point in it is the avoidance of secondary decompositions as a conse-

[1] Vollert, Festschrift.

quence of the reduction of the temperature required for the distillation. A consequence thereof is the substantially smaller separation of coke, which causes the production of liquid residues which can easily be withdrawn. In this manner a rapid emptying and recharging of the still is made possible and a double to triple utilization of the still in the time which was previously required for one distillation. The number of stills is thereby considerably reduced. Webau has now 35 of them (formerly more than 70).

The distillation in a vacuum further equalizes the actions of the tensions and the vapor densities of the hydrocarbons (the former decrease, the latter increase with each CH_2) and thus makes possible a sharper separation with a speedier procedure of the operation.—Webau has three distillation buildings, in the main building there are distilled tar and heavy tar oil and their residues in 26 stills; a second building contains seven stills for the distillation of light oils and two for their residues. In the third building four stills work up the products of the treatment of the mineral oils with chemicals. The last mentioned stills do not operate under a vacuum.

The main building is 84 meters long and 12.5 meters wide; the 26 stills are located beside each other, the fireman's stand is covered and carries on the ceiling the track by which the fuel coal arrives into the fireman's stand by means of charging funnels. The mason work of the stills is [fol. 1403] separated from the distillation room by a wall. It contains, arranged beside each other, 30 coolers, 26 for 26 stills, and four for cooling the Koerting air aspirators, which serve for the production of a vacuum during the distillation. Each still has two receivers, which, being alternately connected to the still and the air aspirator, receive the distillate. As soon as a receiver (about 150 kg.) is filled, the above-mentioned connection with the other receiver is made, which now receives the distillate. Until this is filled, the first one is emptied by opening the cocks and after emptying is again ready to take the place of the other receiver. A mercury vacuum meter, mounted on the cooler, indicates the vacuum in the still, which, when distilling the

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[2] In recent times the vacuum distillation has also been used for the distillation of sea water on steamships. Chem. Ztg. 1889, 62.

paraffin-containing portions, must be 40-50 cm. mercury. The cooling worms are all of cast iron, have 65 mm. diameter and a cooling surface of 8-10 square meters and are built into iron coolers (1.55 by 1.30). The receivers empty into pipe lines, which lead the distillates into tanks where they remain until further treatment. An essential advantage of the method is also that it takes place in a closed vessel and that the removal of the solid residues, the "decoking" is reduced to one-quarter. The troubles formerly caused by the distillation gases and vapors to the workmen—particularly inflammation of the eyes—have ceased completely.

The stills for tar (9) and for heavy oil (6) have at the deepest point a discharge cock, through which the residue by means of a pipe line, is emptied into the residue tanks, of which there are three. The residue stills are filled from the residue tanks by means of compressed air and are distilled off to dryness (to coke). The distillation of the tar residue takes place over lime. The stills for the distillation of the light oils are provided for the purpose of a sharper separation of the distillates with columns (of 2 meters height), similar to those used in the apparatus for spirit distillation. The distillation of the light oils takes place over caustic soda. After the first separation of the tar by means of fractional distillation into crude oil and crude paraffin masses the mineral oils require, apart from the mixing process (see below), according to their use and required purity, a twice, three times or four times repeated distillation. At the second distillation there result already light gas oils as salable products, while the third distillation furnishes benzine, illuminating or solar oil, cleaning oil, light and dark gas oils. The latter result besides fatty oils also [fol. 1404] from the fourth distillation. The procedure of distillation takes place as well for reasons of oil refining as also in order to concentrate and obtain the paraffin contained in solution.

A distillation process, which has for its object the production of light oils by means of the decomposition of heavy, low-valued oils, is the distillation under increased pressure. (Germany Patent 37728.) The process (originating with the author of this pamphlet) is carried out in Webau with two apparatus. As the market for gas oils has improved, a more extended utilization of the process in the immediate

future is not to be expected. However, the literature referring to it may be indicated.

(Jahresber des Technikervereins der sächs-thüring.
Mineralöl Industrie, 1887, p. 17, etc.
Dingler's polyt. jour., 264 p. 336.
Dingler's polyt. jour. 268 p. 88.)

The process has also been extended to heavy German crude oils, to residues of the manufacture of stearin and has been used by Engler to prove experimentally the genesis of petroleum by the decomposition of the fish residues under high pressure.

(Dingler's polyt. jour., 269, p. 137;
Dingler's polyt. jour., 271, p. 516.)

The experimental part of the investigation has been carried out in Webau with the two pressure distillation stills. The process was distinguished by the award of the gold medal at the concours international in Brussels in 1888.

From the residues of the mixing plant (which will be mentioned below) portions come also to distillation, which however does not take place in a vacuum but with the admission of superheated steam at the bottom of the still. For this work there are working in Webau four stills, which produce per month about 600 Hkg. (100 kilograms) oil of creosote and 500 Hkg. Asphalt. The latter is pressed out from the stills with compressed air directly into forms.—The distillation with steam without otherwise heating the still (the so-called blowing off) is principally used in the production of the lightest oils (benzine) and for this purpose there is provided a special still (with vacuum appliance). In the tar and oil distillation proper (in a vacuum and over the open fire) distillation does not take place with the help of steam. The introduction of steam into the upper portion of the still, which is customary in some factories, seems de- [fol. 1405] void of purpose in the vacuum distillation, a distillation with the help of steam—introduction from the bottom of the still—has as a consequence a lesser yield of paraffin, as has been shown by experience.

The distillation is supplemented by the mixing process, the treatment of the products with sulphuric acid and caustic soda. Both chemicals are used in varying concentration,

the first as such of 66° and 50° Be = 1.842 and 1.53 spec. gr. as well as occasionally in the form of fuming sulphuric acid; the caustic soda solution of 32-40° Be = 1.357 spec. gr.— The mixing house at Webau is 25 m. long and 11 m. wide, and contains 10 closed cylindrical vessels, which have peep holes in the cover. The vessels are of wrought iron lined with rolled lead. The chemicals are contained in pressure kettles, which are located in the floor and are pressed into measuring vessels by means of compressed air, which are located higher than the feed line into the mixing vessels. The mixing vessels stand upon columns 3.5 m. high and carry in the middle of their circumference an iron ring, which is riveted to an iron floor, by means of which the whole plant is separated into two rooms, located above each other. The upper room is reached by outside iron stairs, the roof is a roof of corrugated iron. The peculiar substructure allows an abundant lighting of the outlet valves. Below the vessels there run the conduits which receive the mixed products, that is, the chemicals containing the tarry products which settle on the bottom and conduct them further. Each mixing vessel has a capacity of 18000 kg., that is, the charge of 6 or 9 stills and the latter are filled by simply opening the outlet valve provided on the mixing vessel, because the mixing vessels are located at sufficient heights. The mixing takes place by means of air pumps or by the introduction of air.

The mixing house in Webau is well ventilated, because the pillars of the building are all constructed as ventilation shafts and the close vessels open into a wide pipe line, which is connected to an exhaustor.

For running the entire electrically lighted plant, in which there are treated daily about 2500-3000 double hundredweights of mineral oils of all kinds, there are only required two operators, one in the day and one in the night.

The treatment with sulphuric acid removes from the mineral oils the basic bodies and dissolves particularly high boiling unsaturated hydrocarbons and resins. Also a par- [fol. 1406] tial oxydation is effected, which is made apparent by the generation of sulphurous acid. From the basic bodies or their sulphuric acids solutions respectively, the author with Riehm, Höeland and Scheithauer, has isolated a number of bases of the pyridin series. The

pyridin itself is lacking, but a series of picolines have been produced in pure form.

Chinolines and akridines have not been found by the author.[1] When using concentrated acids the mixed product results black and thickly — liquid. It is then decomposed in closed vessels with cooler attached by means of steam introduced, the waste acid is drawn off and the precipitated resins are then distilled with superheated steam. (s. p. 13.)

[fol. 1407] Translation of Petitioner's Exhibit No. 247

Jahresbericht Des Techniker—Vereins—Der Sächsisch—Thüringischen

Mineralöl-Industrie Für 1887

P. 17

Dr. Krey: On pressure distillation (German patent 37728).

The output of our domestic industry in heavy paraffin oils, which can only be used for the manufacture of cheap lubricating media (axle grease, etc.) and particularly for the manufacture of gas (fatty gas), increases from year to year. The offers of such oils from other countries also increase from year to year; England and Russia, Galicia and Rumania capture our gas oil market in foreign countries and in the interior the petroleum distiller, who at the time is only able to obtain very meager yields of illuminating oils from the poor domestic crude product, appears as a notable competitor.

With the intention of finding another use for the heavy gas oils than that indicated by their name, I undertook a series of experiments, which, carried out from October 1885 to February 1886 in the laboratory of the Webau factory, led to a process, which was patented on February 27 in the German Empire and several foreign countries,

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[1] Prof. Dr. Döbner in Halle a/S is at present occupied with an investigation of the high-boiling nitrogen-containing brown coal tar bases.

and which then since the fall of 1886 has been carried out in practice at the Webau factory. I may be permitted to [fol. 1408] describe to you today this process, which found another use for the heavy oils by working them up into light oils (Benzin and illuminating oil), lubricating oils with higher viscosity than is possessed by the brown coal tar oils, or asphalt oils by distillation under higher pressure. The circumstance that the process can also be applied with success to crude petroleums and their residues, the yield of which in illuminating oils is increased thereby by approximately one-half of the present yield, is also of help in the endeavor to decrease competition in the gas oil market also from that quarter. The "pressure distillation," in order to briefly designate the operation, is still further applicable to oil gas tar and its derivatives, to the hydrocarbons which are found in the residues of the stearin manufacture, to the resin oils, etc., and is no doubt capable of still further extension, and I am at present still occupied with corresponding investigations in different directions.

The apparatus, of which I make use in the distillation under higher pressure, consists of still condensing worm and receiver. Between still and condensing worm there is inserted a special valve, by which the process of operation is regulated. The cover of the still is strongly concave carries a safety valve, filling pipe—through which also the emptying of liquid residues takes place—and a manometer with luminous dial, which must be visible from the stand of the operator. The still itself—of cast iron—is in its form more cylindrical than the usual distillation stills and must be of such a nature, that at red heat (temperature of the contents 400-450° C) it can stand a pressure up to 10 atmospheres. For practical purposes I have chosen the still with a lesser capacity than the usual one—500 kg.—and am very much satisfied with the dimensions of the apparatus thus obtained. One can estimate to work up 2½ charges with such an apparatus in 24 hours, that is 25 hundredweights, and connects then suitably 2 alternatingly operating stills to a common condenser. When a still becomes defective, the form and weight of the still allows the lifting-out of the same without destroying the masonry, and also the replacing of the substituted still within a few hours. The life of the stills, presupposing

proper treatment in heating and cooling-off, depends essentially on the material—mixture and dense casting—and must consist rather of soft, than hard, but tough dense iron. Cast steel is not required, as I might mention expressly, in order to correct a view which I have expressed [fol. 1409] formerly; I looked, of course, forward with much interest to the fracture of a still and with me everybody who felt cold chills at the description of a distillation of inflammable bodies at 6 atmospheres pressure. Up to the present we have had two still fractures. The first apparatus, furnished by an autoclave factory and of excellent material, was intentionally not treated carefully. When freshly charged after a pressure distillation of crude creosote with strong separation of coke, the still suffered at 6 atmospheres pressure of the contents during the subsequent distillation a fracture of about 30 cm. length, through which the contents ran into the fire and took fire. The second still was treated more carefully and fractured after short use with a fracture about 40 cm. long. (It may be remarked that the manufacturer replaced it free of charge owing to his conviction that he used unsuitable material. In both instances the fracture of the still—the wall thickness of the still amounts at those places to 40 mm.—caused no greater troubles than an ordinary still fire, in particular there is no greater danger of an explosion and on account of the smaller charge the danger is anyhow materially reduced. The condensing worm I made, with double the cooling surface as compared with the usual distillation, very narrow as far as the diameter of the cooling tube is concerned, from 2″ gas pipes and, moreover, I inserted between cooling worm and receiver—intended for the reception of the distillate—a measuring apparatus, which allows the continuous reading-off of the specific gravity. According to this and the indication of the manometer the operation is conducted and the procedure of the operation is regulated with the above-mentioned valve, which is located between the still and condensing worm. For practical reasons I decided not to make the valve automatic.

After the still is filled, it is heated and treated as under ordinary conditions, until the contents come to boiling after giving-off the water. Then the intermediate valve is closed until the required pressure, which according to

the nature of the oils varies between 2-6 atmospheres, is obtained, thereupon the valve is opened and the heating is so regulated that the pressure remains constant, as well as the specific gravity of the pressure distillate, which is read-off on the receiver. When the march of the operation is properly conducted, the areometer only moves up or down, two or three divisions. One fireman and one distiller operate a whole series of apparatus and as fuel material 0.7 hl. brown coal per 100 kg. of decomposed prod- [fol. 1410] uct is required. Characteristic of the whole procedure is on the one hand that with a properly conducted operation the product of the decomposition is constant as to quality and on the other hand that the operation can be terminated at any instance, without thereby influencing the product—as far as it is distillate. The point of time for finishing the pressure distillation is only of importance for the nature of the residue. When taking-off 25 per cent distillate there remains a thickly-liquid, green-fluorescing oil, with 50-60 per cent a thicker, tar-like oil, specifically heavier than water, and with 80 per cent there remains coke. The distillate is of equal nature when taking-off 25, 60 and 80 per cent and one influences its content in light oil by the pressure used. One is perfectly in a position to obtain a distillate of 0.800 or 0.830. The more distillate one takes from the still, the more increases, of course, the loss by gasification, and when judging the specific gravity of the pressure distillate one must consider that it contains about 1.5 per cent of gas in solution. The gas can easily be drawn off and used for auxiliary heating of the stills. After operating the apparatus for some time and when treating a heavy dark paraffin oil of 0.900 specific gravity I now work with 60 per cent pressure distillate 0.830. There remains 30 per cent residue, the remainder of 10 per cent is lost as water, gas and coke. If the required quantity has been distilled off, the fire is removed, the pressure in the still sinks rapidly and already after 2 hours the residue is pressed out through an inserted pipe which reaches down to the bottom of the still, by means of compressed air, and the still, which is still warm, is immediately charged again. In order to become illuminating oil or benzine, respectively, the pressure distillate, of course, still needs a purification, and the extent of the same is also dependent on the nature of the raw product—

for instance, upon its contents of creosote. The residue represents a thinly-liquid goudron, which can either be sold as such or else can be worked with profit to a useful lubricating oil of 0.960 specific gravity and 10 viscosity (Engler). In the refining one still obtains small quantities of light paraffin oils (cleaning oils) and solar paraffin scales. The paraffin is seemingly in oily solution not substantially reduced in quantity but in quality by the lowering of the melting point. Creosote distills in oily solution still unchanged at 8 atmospheres pressure; however, if crude creosote by itself is distilled under pressure, decom- [fol. 1411] position also occurs, and the splitting-off of hydrocarbons from the oxygen-containing, phenol-like bodies takes place.

The products benzine, light cleaning oil and solar paraffin scales are identical with those of our other manufacture, and I therefore only submit to you today representative samples of illuminating oil and lubricating oil. The refining of course causes still further losses and I include among them the loss of creosote and acid resins. From 100 kg. dark gas oil I obtain (by pressure distillation with subsquent refining)

6 kg. benzine 0.750,
33 " illuminating oil, according to the sample shown,
15 " cleaning oil 0.860,
15 " lubricating oil, according to sample,
0.6 " solar paraffin scales, 30° C melting point,

so that the total loss is about 40 per cent on the gas oil used. After accurate calculation, figuring 0.50 marks amortisation (for upkeep of buildings, replacement of stills) of the total plant per 100 kg. decomposed oil and on the basis of the following prices for the products: 10 marks for benzine and illuminating oil, 11 marks for lubricating oil, 9 marks for the cleaning oil, 30 marks for the paraffin scales, all per 100 kg. including containers f. o. b. factory, I utilize—chemicals and coal prices, etc. are those of the last business year—the dark gas oil in my process at 6 marks per 100 kg. (including containers). Many a car of saxonian gas oil has already gone to other countries at a lower price and we should not be disinclined in view of our

stocks to sell much lower if we could only dispose of it. A burning of the oil by means of the forsunka could never compete with the pressure distillation even at the low prices at which the distillates are valued.

The operation of the pressure distillation is not attended with greater danger in practice than any other distillation of mineral oils; particularly in connection with mineral oil factories their operation is easily installed and does not then require a special governmental permit. The industrial inspection authorities limit themselves to prescribing rules for the practical operation which are in no wise onerous for the same and correspond in the main to those for the operation of autoclaves in dye factories.

The chemist who is interested in the process I must refer to a scientific investigation with which Professor Engler in Karlsruhe is at present still occupied, because the means at our disposal in our laboratory in Webau are not sufficient [fol. 1412] therefor. As far as I have been advised from there up to the present, the illuminating oil as far as boiling analysis, elementary, analysis, ignition point, burning, smell and color is concerned, is characterized as a product equal in value to one of the best of these products; only about 1/3 of the oil in the crude distillate consists of unsaturated, about 2/3 of saturated hydrocarbons. In the beginning of my paper I have already mentioned that also shale oils and petroleums as well as their residues have been successfully treated by the process and I will give some further data which elucidate the action of the pressure distillation on these products. There was subjected to investigation a crude petroleum from Pechelbronn (Alsace) of specific gravity 0.880. 25 per cent of crude oil are distilled off, as usual, the residue is for the purpose of comparison subjected to ordinary distillation and to pressure distillation under 3 atmospheres pressure and only 50 per cent distillate taken off. In the first distillation there is obtained a distillate of 0.868, in the second one of 0.817 specific gravity. According to the boiling analysis of this distillate the one distilled as usual contains up to 190°. 0 per cent, the one distilled under pressure 23 per cent; up to 250 (per cent?)° there boil of the first 16, of the second 51 per cent; up to 300° the proportion is 42 per cent to 83 per cent. In this man-

ner there were produced according to the distillation usual up to the present 35.6 per cent of benzine and illuminating oil, according to the pressure distillation 50.9 per cent benzine and illuminating oil. By the latter was understood the product boiling up to 280°. The increase of yield amounts therefore to 15%, that is about one-half more than before. The yield can be still further increased, if one does not, as in this investigation, work with 37 per cent residue of the crude petroleum, but to a smaller percentage of liquid resid-e or to dryness. From Baku residues, which I have worked repeatedly and on a larger scale, I obtain in the distillation under 3-5 atmospheres 50-58% finished refined benzine and petroleum, besides 15-20 per cent of higher boiling so-called middle oils. Applied to the latter, which also result in the ordinary distillation of crude petroleum in unwelcome quantity, the pressure distillation furnishes also a high percentage of petroleum. The process seems to me capable of extension to still further branches of the hydrocarbon art, and I am still occupied with them, as I have mentioned already in the first part of my paper. But even in the present condition of things the process seems [fol. 1413] to be worthy of attention, which not only in a scientific respect has given us an insight into the nature of hydrocarbons which we did not have before, but which also proves what considerable role the pressure has played in the genesis of petroleum and similar fossilia. For me its importance for our industry lies therein, that in it we possess a means, to bring any desired quantities of unsalable or only at heavy sacrifices salable product into a form capable of being marketed and to regulate supply and demand on the gas oil market. Viewed from this standpoint, the value of 6 marks per 100 kilograms must be considered as one at which our industry can still make a profit. At present prices there is certainly no inducement per se to force the manufacture of illuminating oil, but in any case a good illuminating oil and a useful lubricating oil are more marketable articles of consumption than the best gas oil, if it can be had in such quantities as in our deposits, is to be hoped for in such quantities as from the distilling coals of the future and any other saviour and redeemer from the evil does not appear soon.

[fol. 1414] TRANSLATION OF PETITIONER'S EXHIBIT No. 248

Dingler's Polytechnic Journal

With the Co-operation of Professor Mr. C. Engler, in Karlsruhe; Edited by Engineer A. Wollenberg, in Stuttgart Wocent; Dr. H. Karsf, in Karlsruhe

Volume 268. Year 1888

Article of Prof. C. Engler on the German Petroleum

(Pages 88-90)

D. Working up of the Residues by Pressure Distillation Into Light Oils

(Illuminating Oils, etc.)

Owing to the fact, that the emphasis in the utilization of most of the German petroleums on account of their low contents in illuminating oil, must be laid upon a suitable working up of the residues, and as furthermore the utilization of the same as lubricating oils finds an obstacle partly in their own chemical nature and partly also in the always increasing competition of the excellent Caucasian lubricating oils, another paying utilization must be thought of. As such there offers itself lately the distillation of the same under high pressure according to the patent of Dr. Krey1)

In the distillation of the residues under high pressure, mainly the same products must form themselves as in a dry distillation at quite moderate temperature. In the latter respect experiments have already been made years ago, but without practical result: Thus Vohl has shown already in 1869, that when passing the vapors of heavy oils from bog head coal, plat,, petroleum, etc., are passed through tubes heated to 500-550°, there are formed oils workable into lubricating oil. Unfortunately the process proved too costly and of permanent interest in Vohl's investigations is only the demonstration, that in the oils (fraction 200°) produced by him there are combined the hydrocarbons, $C_{13}H_{28}$, $C_{14}H_{30}$, $C_{15}H_{32}$.

[fol. 1415] A similar thing has been observed by Hayes with American Petroleum and Williard (there) 1, compares the note on p. 597, Vol. 267.

has constructed an apparatus on the ground of these observations to distill the heavy mineral oils under increased pre-sure at higher temperatures. The above mentioned, however, put the greatest emphasis on the increase of temperature.

Krey follows an entirely new principle in his experiments. He has observed, that by distilling heavy mineral oils under pressure, light oils are obtained again and that by variation of the pressure one has it completely in one's hand to produce light oils of any desired nature.

Dr. Krey has subjected in his apparatus some batches of residues from Oelheim and from Pechelbronn crude oil to the pressure distillation; thereby resulted under a pressure of 2-5 atmospheres.

From residues	Per-cent by weight crude distillate	Spec. gr.	Coke residue	Gas loss
From Oelheum	75	0.800	17	8
" Pechelbronn.	60	0.785	31	9

Whereby it must be observed that the coke residues remaining in the still with the Oelheum residues were completely carbonised, while those of the Pechelbronn residues appeared only asphalt-like, so that the yield from the latter could have been increased somewhat by continuing the distillation.

A fractionated distillation, carried out with 100 cc., i. e., with 80 gr. (Oelheim and 78.0 gr. (Pechelbronn) respectively, according to the method described formerly, gave the following results:

[fol. 1416]

High-pressure oil from residues of	Commencement of boiling	Up to 100° cc.	Up to 100° gr.	100-150° cc.	100-150° gr.	150-200° cc.	150-200° gr.	200-250° cc.	200-250° gr.	250-300° cc.	250-300° gr.	Above 300° cc.	Above 300° gr.
Oelheim	45°	11.3	8	14	10.4	22.7	17.8	24.7	20.3	13.7	11.7	18.6	11.8
Pechelbronn	45°	11.0	7.4	19	14.7	23	17.7	28.3	23.3	11.3	9.8	7.4	5.6

In total they contained in the three principal fractions:

	Under 150° % by vol.	Under 150° % by weight	150-300° % by vol.	150-300° % by weight	Above 300° % by vol.	Above 300° % by weight
High Pressure Oil from Oelheim	25.3	23.0	61.1	62.3	13.6	14.7
High Pressure Oil from Pechelbronn	30.0	28.2	62.6	64.7	7.4	6.1

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[fol. 1417] In the product obtained according to the above-described method we have therefore on mixture of light essences with much illuminating oil and only little heavy oils.

The quantity at disposal was not sufficient to isolate individual hydrocarbons by fractional distillation; in order, however, to obtain a basis for the answer of the question, whether the high pressure distillate consists principally of unsaturated (C_nH_n) (Aromatic) hydrocarbons, three principal fractions of the same were shaken three times successively, the first time in the cold, the two following times at 40°, with three volumes of English sulfuric acid, which contained 20 per cent of fuming acid. There resulted a decrease of the oil layer expressed in volume per cent of:

Pressure Distillate of Fraction

	100-150	150-200	200-250°
Oelheum residues	27	40	40
Pechelbronn residues	25	37	38

As in the last treatment with sulfuric acid an appreciable dimunition did no more take place, the differences from 100 must be considered as saturated hydrocarbons, partly perhaps as hexahydrides and therefore the pressure oils consist principally of such. In accordance with this is the low specific gravity of these oils, at least of the lower boiling fractions. The following specific gravities (at 16°) were found.

From Residues Fraction

From	Under 100°	150-150°	150-200°	200-250°	250-300°
Oelheum	0.1965	0.7460	0.7865	0.8315	0.8590
Pechelbronn	0.6970	0.7525	0.7805	0.8256	0.8570

Noticeable in these results is the great difference of the specific gravity of the lowest and the highest boiling fractions. Only the further chemical investigation of these oil can show to what this is due.

In order to examine the pressure oils with respect to their value as illuminating material, there was first determined the ignition point of the total distillate boiling before 300°, and as this proved too low, considerably below 21°, the oils boiling below 125° from the "illuminating oil

fraction'' (everything boiling below 300°) were distilled off. The loss occasioned thereby is about half of the portions boiling below 125°, so that the yield of illuminating oil in both pressure oils amounts to 75 per cent in round numbers. The illuminating oils thus obtained by distilla- [fol. 1418] tion and then chemically purified show the ignition points 22.5° (from Oelheum residues), and 26.5 (from Pechelbronn residues). According to the result of the photometric examination a small portion of the oil boiling above 300° might still be included in the illuminating oil. It is self evident that also the light essenses boiling below 125°, obtained as by-products, can be well disposed of as ligroin, benzine, petroleum either, and the residue serves as fuel.

A high pressure oil produced in the same manner from Baku residues under a pressure of 4 atmospheres gave in per cent by weight:

Yield	Spec. grav.	Coke residue	Gas loss
76	0.836	14	10

The crude distillate gave often chemical purification with sulphuric acid by distillation an illuminating oil with

Yield	Spec. gravity	Ignition point
61 per cent by weight	0.818	34°

This illuminating oil was, as well as those from the residues of Oelheim and Pechelbronn water clear and easily mobile and gave with fractionated distillation of 100° according to the method used before the following main fractions in volume per cent:

Up to 100°	150-200°	200-250°	250-285°	Rest
12	38	39	8	3

We have also in this case a very good illuminating oil, with respect to its fractional parts. As to how far it corresponds to these expectations in practical use, must be shown by the photometric examination, but a favorable result of the same is hardly to be doubted.

In this method of working originated by Krey we have a novelty, to which much attention must be paid in the utilization of our mostly very heavy German petroleum and particularly of those residues, which are not suitable for working into lubricating oils, as i. e. almost all the Alsatian ones.

[fol. 1419] TRANSLATION OF PETITIONER'S EXHIBIT No. 249

II. On the Decomposition of Solid and Liquid Hydrocarbons by Pressure and Heat

Inaugural Dissertation of the Faculty of Mathematics and Natural Sciences of the University of Freiburg, Switzerland, for Obtaining the Doctor's Degree

Presented by Josef Jacunski, from Wilno

Freiburg, Switzerland: Printed by Gebrüder Fragniere.
1898

II

On the Decomposition of Solid and Liquid Hydrocarbons by Pressure and Heat

The decomposition process of solid paraffin and the high boiling hydrocarbons at higher temperature and under pressure, as well as the condition under which the process for obtaining lighter hydrocarbons proceeds best, has been little investigated up to the present, though an insight into these conditions which are undoubtedly very complicated is of great interest for science as well as for the industry.

The two methods of which use is made in the petroleum industry for working up the petroleum residues to illuminating oil, are the so-called cracking process and the process of high pressure distillation according to Krey (German Patent No. 37728).

While the so-called cracking process consists in the [fol. 1420] superheating of the high molecular hydrocarbons of the residues by the contact of the same or their vapors with the hot walls of the distillation apparatus, the

process according to Krey has for its purpose to decompose the residues into lighter hydrocarbons by heating in a cast iron still under varying pressure of 4-10 atmospheres.

The inner chemical processes, which are at the bottom of the formation of the newly generated hydrocarbons, are not known up to the present. Beside the remarkable observations of Krämer and Spilker, than by Zaloziecki, which gave attention to this question, there are available up to the present only the experiments of Thorpe and Young[1]) and lately the investigations of Engler[2]) and his pupils (Jezioranski, Grüning and Schneider) which are adapted to lead to the solution of the question.

As the residues of the petroleum industry, which are subjected to one or the other technical process, consist without doubt of high molecular hydrocarbons, it must be imagined, that they can decompose into lower hydrocarbons in a different manner at higher temperature with or without pressure. A splitting-off process takes place, which can proceed in highly complicated manner according to the conditions which obtain in the decomposition. There are formed decomposition products of paraffinic, olefinic or cylic character, which with respect to the split high molecular hydrocarbons represent either split-off piece of equal or of different size in connection with which, of course, there must also be considered the migration of the hydrogen, the splitting-off of hydrogen and even the separation of coal in the form of coke.

As the decomposition products which appear in the first place are partly very unstable compounds, the subsequent condensation and dissociation process makes the procedure of the reaction always more complicated, so that no certain picture can be obtained of the primarily occurring processes, which continuously are changed in quick succession by decomposing and synthetic reactions.

It is of course self-evident that with these processes which have just been mentioned the temperature as well as the pressure play an essential role and the influence of these conditions finds also its expression in the investigated

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[1]Ann. of Chem. and Pharm. 165, 1.

[2]Berichte der D. chem. Ges. 30.

products of one or the other process in a very decisive manner.

[fol. 1421] Also as far as the places of the decomposition are concerned, at which the high molecular hydrocarbons decompose into smaller equally or differently large paraffinic or olefinic split pieces, there is just as little clearness as concerning the influence which is exerted on the splitting place by pressure and heat.

While Haber (habilitation volume, Karlsruhe 1895) showed in the pyrogenic decomposition of lower aliphatic hydrocarbons, that the primary products of the decomposition are smaller paraffinic and larger olefinic split pieces, Thorpe and Young observed in the decomposition of solid paraffin under pressure and heat on the contrary splitting in the middle of the chain, into olefins and paraffins of equally great content in hydrocarbons, of which they could prove and isolate different representatives of both classes. They distilled for example 6 grams of pure paraffin melting at 41.5° C in a closed tube bent in the shape of a V, back and forth.

After repeating this operation twelve times, the larger portion of the substance remained liquid at ordinary temperature and the paraffin had been changed over into split products of lower carbon content.

Further experiments in order to find out under which conditions this decomposition process of the paraffin occurs most easily, have not been carried out by Thorpe and Young. They write concerning this point: "Though there is no difficulty to reach in this manner the final changing over of solid paraffin into liquid products, the speed of this change seems to be dependent upon conditions which we cannot yet state to have sufficiently ascertained."

From this point of view therefore it appeared necessary to repeat the experiments of Thorpe and Young, because it could be presupposed that by the use of higher pressure and with increased temperature there should be effected already in the first distillations a quick decomposition into liquid portions, whereas in their experiments the pressure was reached only gradually from distillation to distillation by the splitting off of gaseous split pieces.

Further Thorpe and Young have also extended this experimental arrangement to the decomposition of liquid hy

drocarbons of the boiling point 250° C., but in spite of many experiments always with a negative result.

On the basis of these experiments they believed to be able to make the assertion, that only paraffins of high boiling [fol. 1422] point, which are solid under ordinary conditions, are capable of a decomposition in this manner, which seems to be dependent upon the more complicated composition of the solid paraffin, but that a mixture of paraffinic and olefinic hydrocarbons of the boiling point 255° C. is not subject to this decomposition. When Thorpe and Young arrived at this result after distilling the paraffin mixture twenty-one times to and for, they started in the carrying out of their experiments from the presupposition, which is not quite correct, that the decomposition of the hydrocarbon is connected more with its boiling temperature than with the absolute temperature. My experiments showed on the contrary, that also lower boiling hydrocarbons are decomposed when by increasing the pressure the temperature is increased to such a degree, that the boiling temperature is exceeded.

The Decomposition of the Solid Paraffin

Six grams of solid paraffin melting at 60° C were enclosed in a 2-leg soda glass tube, the two legs forming an angle of 160-170°. The two legs were introduced into two oppositely located bomb furnaces, the leg containing the paraffin (for example the right one) was heated to 350° C, the other empty leg to 150° C. In order to have higher pressure in the tube from the start, one ccm. of ligroin (boiling point 30° CO was added.

After twenty hours the paraffin had distilled over. The distillate was after cooling of buttery consistency and white. The left leg was then somewhat turned up end by heating it the paraffin was melted back into the right leg. After further heating of twenty hours the distillate was already more thinly liquid and had acquired a light brown color. This operation was then repeated several times. After the sixth distillation the distillation product was dark brown and only after the seventh it remained liquid at ordinary temperature. When opening the cooled-off tube there was a moderate pressure present and the empty leg, which had contained the paraffin at the beginning of

the distillation, showed in its interior a not inconsiderable quantity of coke-like separations.

The experiment was now changed in such a manner that the leg which contained the paraffin was heated at 500° C. and the empty one to 250° C. Thereby it was shown that the process of decomposition after 24 hours' heating had [fol. 1423] already progressed considerably further than compared with the former experiment, because the paraffin distillate formed now already a dark brown semi-liquid mass.

After repeating the operation once more, I obtained a darkbrown distillation product which was thinly liquid at ordinary temperature. When opening the tube there was noticed a not inconsiderable pressure, so that the gas issued from the capillary rather energetically. The content of residual coke from this experiment was the same as in the former.

From the results thus obtained it follows without equivocation that the process of the decomposition is very much dependent upon the pressure and the temperature and that with favorable regulation of the pressure and the heat the decomposition takes place more quickly than if the pressure is generated only little by little, from distillation to distillation, by the gradual formation of gaseous and easily volatile decomposition products.

The Decomposition of the Liquid Hydrocarbons

After these preliminary experiments with solid paraffin there could be expected already apriori the decomposition also of liquid hydrocarbons of boiling point 250-300°, which under the experimental conditions of Thorpe and Young had even resisted decomposition when distilled twenty-one times, if only care was taken to get the necessary pressure and therewith also sufficiently high temperature.

As Thorpe and Young in their experiments for the decomposition of the liquid hydrocarbons did not generate the suitable pressure in the tubes and only obtained negative results for this reason. I laid particular emphasis in my experiments upon the generation of the suitable pressure.

For this purpose there was added each time to the contents of the tube 1 ccm. of ligroin (boiling point 30° C);

furthermore both legs were heated to different temperatures, in contradistinction to the experiments of Thorpe and Young, which only exposed one leg to a high temperature. I also operated with always increasing quantities of substance.

A. Decomposition of a Russian Lubricating Oil from Baku of Nobel, Sp. Grav. 0.90288

About 15 ccm. of the oil of sp. grav. 0.90388 with 1 ccm. ligroin (boiling point 30° C) were enclosed in a 2-leg, [fol. 1424] slightly bent soda glass tube 90 cm. long. As it was observed that some ligroin always evaporates from the tube, which creates difficulties when melting the same together, by its inflammation, the ligroin was enclosed in a capillary tube, and the opening in the capillary was closed with some solid paraffin. The tube charged in this manner was inserted into two oppositely located bomb furnaces and both legs were heated, the one to 450° C and the other to 150° C. After heating for 25 hours, there resulted a rather thinly-liquid distilate.

In order to decompose the oil still further, 25 ccm. of the lubricating oil were heated with 1 ccm. ligroin (boil. pt. 30° C in the same manner, one of the legs to 500° C, the other to 125° C. After 24 hours heating a thinly-mobile liquid had collected in the leg heated to 125° C.

When opening the tube there escaped a large quantity of combustible gases and in the leg which had been heated to 500° C and which had originally contained the substance, a considerable quantity of carbon had separated.

Determination of Specific Gravity and Proof of the Polymerisation of the Distillation Product

The distillate obtained in this manner showed on the Mohr scale a spec. gr. of 0.8398 at 15°.

From this result it could already be deduced that the decomposition must have been a rather far-reaching one, because the spec. gr. of the crude oil had been 0.90388. The distillate was dark brown and clear. After two days the liquid had clouded somewhat, and showed a bluish flourescence and with this change there had occurred an increase in spec. gr. to 0.8440 at 15° C, a circumstance which points in the direction of polymerisation phenomena.

Another portion of the liquid distillate showed after opening the tube a specific gravity of 0.8609 at 13° C and after one day it was already 0.826 at 13° C.

Production of Larger Amounts of the Decomposition Products of the Lubricating Oil

After I had succeeded in obtaining the decomposition of the oil by means of pressure and heat, it should be of interest to investigate how far the decomposition process takes place in general and which components are contained in the products of distillation. In order to obtain a sufficient [fol. 1425] amount of the liquid distillate, the lubricating oil was heated in the required amount of tubes, each of which was charged with 25 ccm. substance.

The leg containing the substance was heated to 500° C, the other one containing the distillate was heated to 110° C. From each tube I obtained about 20 ccm. distillate, the rest had changed over into gases and carbon.

Fractionated Distillation of the Liquid Product

One hundred ccm. of the liquid product was subjected to a fractionated distillation after the well-known and generally used method of Engler.

It gave the following results:

Beginning of Boiling 47° C.

Fraction of	ccm.
47- 75° C.	7.5
75-100° "	4.0
100-125° "	4.8
125-150° "	6.7
150-175° "	8.0
175-200° "	6.0
200-250° "	20.0
250-300° "	19.5
Above 300° C.	23.5
Total	100.00

Determination of the Olefines and Paraffines

To determine the olefines I used the bromation method, which is already mentioned in the paper of Thorpe and

Young, and by which they were able to determine and isolate olefines and paraffines. It has later been used again by Engler with some modification (either dilution), and has lately been particularly extended and recommended by Heusler[1]).

It depends on the fact, that when bromine acts in the cold upon a mixture of unsaturated and saturated hydrocarbons, only the olefines are attacked at first, that is to say changed over into bromine addition products, whereas the [fol. 1426] paraffin in hydrocarbons remain unchanged under these conditions and are only changed over into bromine substitution products with the generation of hydrobromic acid when all the olefines have been saturated by bromine. The two chemical processes can be separated when the reaction is interrupted at the proper time, as soon as the generation of hydrobromic acid, which can easily be noticed, shows the beginning of the substitution. From the quantity of bromine used a conclusion can then be drawn concerning the quantity of the olefines contained in the oil and their bromine derivatives can be separated by vacuum distillation.

The liquid product obtained by pressure distillation was subjected to a fractionated distillation and the portion which passed over from 47 to 250° C—there were about 100 ccm—was dissolved in 200 ccm. absolute ether and was subjected to bromation while cooled to about -18° C.

The bromine which was added drop by drop from a burette, was at first absorbed immediately by the oil and only after some time hydrobromic acid began to be generated. The consumption of bromine up to this point was 19 ccm. If in the mixture, which boils between 47 to 250° C, there is assumed as an average an olefine $C_{16}H_{32}$ (boiling point 170° C[2]), there results from the bromine consumption of 19 ccm.—60 gr. as an average about 52 per cent olefines.

More exact data on the percentage content of olefines would be obtained if individual representatives of this class would be fractionated out and subjected to broma-

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[1] Ber. der D. chem. Ges. 25, 1670 and 28, 490.

[2] Hexadecylen, $C_{16}H_{32}$ "Ceten" Boiling point 240° C at ordinary pressure.

tion. For the present purpose the above-mentioned determination was sufficient.

In order to remove bromine and hydrobromic acid, a strong current of air was conducted through the liquid, which was colored wine yellow, and the oil was then subjected to water vapor distillation. At first there passed over the unchanged oils, paraffines and naphtenes, in quantity about 21 ccm., which were characterized by their swimming on the water; then followed the bromides which sink in the water.

The first 25 ccm. of the bromides distilled undecomposed, while the high boiling bromides which were still present in the flask began to decompose. As residue there remained in the flask a resinous black mass, which did not admit of further working.

In order to separate as well as possible the unattacked [fol. 1427] oils, paraffines and napthenes, from the bromides they were subjected to water vapor distillation a few more times, separated from the water, dried with calcium chloride and the dry oil was heated 12 hours with metallic sodium with a return condenser in the oil bath in order to destroy the last traces of bromine compounds.

Elementary Analysis of the Liquid Distillate Which Boils Below 250° C.

A. Before Bromation

I. Substance used = 0.0910 gr. gave:
0.2865 gr. carbonic and
0.1121 gr. water.

These figures correspond to:
C = 85.86%
H = 13.68%
99.54

II. 0.064 gr. of substance gave:
0.2020 gr. carbonic acid and
0.0791 gr. water.

Calculated therefrom:
C = 86.08%
H = 13.73%
99.81

$C_{10}H_{20}$ requires:

85.72% C.
14.28% H.

B. After Bromation

I. 0.1272 gr. of substance gave:
0.3977 gr. carbonic acid
0.1643 gr. water.

Calculated therefrom:
C = 85.27%
H = 14.35%

99.62

[fol. 1428] II. 0.0793 gr. of substance gave:
0.2486 gr. carbonic acid and
0.1020 gr. water.

Calculated therefrom:
C = 85.33%
H = 14.27%

99.60

From the results of the analysis and the quantity of bromine used it is shown that the pressure distillate contained considerable quantities of olefines and saturated hydrocarbons. Owing to the lack of material the determination of benzol hydrocarbons and napthenes could not be carried out.

B. Decomposition of the Petroleum of Gemsah (from the Coral Cliffs of the Red Sea)

In order to complete the investigations concerning the decomposition of the liquid hydrocarbons by means of pressure and heat, the petroleum, which has already been investigated before, from Gemsah of spec. gr. 0.986 at 18° C. was subjected to the action of pressure and heat.

25 ccm. petroleum were heated with 1 ccm. ligroin (boil. pt. 30° C.) in a slightly bent 2-leg soda glass tube 90 cm. long, the one leg to 500° C. and the other to 150° C.

After 24 hours' heating the distillate had collected as a thinly mobile blackish brown liquid, the greater portion of which was lost as gas when opening the tube, with strong foaming.

In the tube there remained only a small quantity of liquid and very much asphalt, which had separated on the walls of the tube as a shining, long fibre deposit.

This phenomenon can be explained in the following manner:

The petroleum is decomposed under the action of the high pressure and the heat into hydrocarbons which are gaseous at ordinary temperature but which remain in liquid condition under the high pressure.

25 ccm. petroleum were again subjected to distillation in the same manner and the one leg was heated to 350° C., the other to 100° C. After 20 hours' heating the distillate had collected as blackish brown mobile liquid, which re- [fol. 1429] remained after opening the tube in a quantity of about 20 ccm.; the rest was lost as gas and carbon.

Fractionated Distillation

In order to obtain an insight as to how far the decomposition of the petroleum had proceeded in this case, 50 ccm. of the liquid product obtained were subjected to a fractionated distillation according to Engler's method.

The fractionated distillation gave the following results:

Beginning of Boiling 51° C.

Fraction of	ccm.	Calculated to 100
51-100° C	6.8	13.6
100-150° C	3.0	6.0
150-200° C	5.0	10.0
200-250° C	8.5	17.0
		46.1%

Almost one-half (46.1%) of the distillate boils under 250° C., whereas the crude petroleum begins only to b-il at 260° C.

Determination of the Olefines

In a preceding section of this paper I described the bromation method which was used for determining the olefines.

According to Engler's experiments also the behavior of sulphuric acid of different concentration can be used for determining the olefines.

If a mixture of olefines, paraffins and other hydrocarbons is shaken with concentrated sulphuric acid, there takes place essentially -almost exclusively[1]) an absorption of the olefines by sulphuric acid; other hydrocarbons act almost indifferent towards this acid.

This fact gives a means of investigating whether the petroleum contains olefines and in what quantity.

The liquid product from the pressure distillation of the petroleum was subjected to fractionated distillation and the portion which boils below 250° C. was treated with concentrated sulphuric acid.

[fol. 1430] 10 ccm. of distillate were shaken with 30 ccm. of English sulphuric acid in a graduated burette for about half an hour and were then allowed to stand for 3 hours.

Of 10 ccm. distillate 3.1 ccm. were absorbed by sulphuric acid. The rest of 6.9 ccm. was further shaken with 2.5% fuming sulphuric acid and a decrease of the distillate to the amount of 0.2 ccm. was found; 6.7 ccm. of the distillate remained unattacked. This decrease of volume, i. e., 3.3 ccm., corresponds very closely to the contents of the distillate in olefines.

[fol. 1431] TRANSLATION OF PETITIONER'S EXHIBIT No. 250

The Decomposition of Heavy Mineral Oils by Heating

Inaugural Dissertation of the Faculty of Mathematics and Natural Sciences of the University of Freiburg (Switzerand) for Obtaining the Doctor's Degree

Presented by Herman Gruening, of St. Petersburg

Freiburg (Switzerland): St. Paulus Printing Office. 1898

The present investigation was made in the organic laboratory of the Technical University at Karlsruhe at the suggestion of Privy Counselor Professor Dr. C. Engler.

I may be allowed also at this place to voice my heartiest thanks to my honored teacher for the interest with which he

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[1] Compare Lehmann Inaug. Dissertation. Freiburg, Switzerland, 1897.

followed the work as well as for his many valuable advices during my studies. I am also greatly obliged to Dr. Camps for his manifold encouragement.

It is an agreeable duty to me to also thank Prof. Dr. A. Bistrzycki for the interest he has taken in my studies in Berlin as well as in this investigation.

Introduction

The petroleum occurring in nature is subjected to a refining in order to convert it into salable petroleum. For this purpose it is distilled in large stills of cast or wrought iron. In this operation easier boiling portions pass over first, which, as far as they boil up to about 150° C, come into trade under the name of benzine, petroleum, ether, etc. When the distillation is carried further, oils of higher specific gravity pass over, which when working American crude oils are collected up to about 300°, with Russian oils up to about 275°, and after a chemical purification process (treatment with concentrated Sulphuric acid, caustic soda and water) are used as illuminating oil.

The portions boiling above 275° or 300° respectively, which we designate by the name "residues" find application [fol. 1432] for quite a long time partly as fuel and partly for the manufacture of lubricating oils and paraffine. In later times, however, they were also worked up into illuminating oil by superheating, in the so-called Cracking process.

In regions, where the usual fuel materials are only procurable with comparative difficutly, the residues are used as welcome substitute for them—i. e. for heating purposes. Their combustion takes place in the so-called "forsunka." These apparatus are based on the principle of atomising the residues by means of steam and combustion of these vaporized masses. The atomization by means of a current of air has shown itself unpracticable, because a strongly smoking flame is produced in this process and therefore a portion of the carbon does not fulfill its purpose of heating. On the contrary the atomization and also the combustion when using water vapor are obtained to such a high degree that no separation of soot takes place.

By distillation with water vapor tension there is, obtained from the residues, f. e. in Baku, a product which comes into the trade as lubricating oil. In America, where the petroleum is on the average richer in paraffine, the residues are also worked up to paraffine, besides lubricating oil. The

latter is separated from the heavy oils by cooling and obtained by pressing.

The process of "cracking" is an old one as far as its principle is concerned, but it only finds in more recent times more extended application for the working up of the residues. It depends on the decomposition of the high molecular hydrocarbons by superheating. An influence on the procedure of the reaction can be exerted either by varying the temperature or by suitable choice of the pressure and by the help of substances such as lime and coke, over which the vapors are conducted during superheating.

Breitenlohner [1]), who it seems must be considered the originator of the "cracking," causes, in order to produce the splitting of the high molecular hydrocarbons of the residues, not oils but the vapors of these oils to pass through superheated draw-off tubes. In a strongly heated kettle the residues are evaporated and the vapors are conducted through a heating device which is connected to a good cooling plant.

As the distillation still and the decomposition apparatus are heated independently, one is able, as required to pass a [fol. 1433] stronger or weaker current of vapor through the heating tube and to regulate the heating of the same.

Vohl [2]) tried first a decomposition of heavy mineral oils from different localities by superheating in the presence of strongly-acting reagents, f. i. of sulphuric acid, caustic soda and incandescent lime, but without favorable results. Also he comes back to the use of high temperatures (low red heat) and uses when studying some high aliphatic hydrocarbons the apparatus of Breitenlohner with the modification that he fills the heating tube, for the purpose of a greater surface of decomposition, partly with iron turnings.

While the different proposals to allow porous bodies—such as lime or coke—to act upon superheated vapors, have not succeeded, there have been developed later two processes, one of which is the pressure process according to Krey [3]) and the other the above-mentioned simple cracking process.

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[1] D.P.J. Vol. 167, 378; Vol. 175, 392.

[2] D.P.J. Vol. 177,69.

[3] Germ. Pat. No. 37728.

Krey's process is briefly the following: In a strong cast iron distillation still the residues are heated under a varying pressure from 4 to 10 atmospheres. The dome of the still is closed in front of the condenser by a valve, the pressure of which against the issuing oil vapors is regulated by loading it on the outside. Then follows the cooling worm for the condensation of the distillates. The different distillates then go through a small glass cylinder in which their specific gravity is ascertained constantly by an aremeter swimming therein, whereupon they are collected in a cylindrical receiver of boiler iron.

The other process, called "cracking" in the narrower sense, consists in a superheating process, which affects a decomposition of the high molecular hydrocarbons of the residues and is based on the contact of the oils or their vapors with the hot walls of the distillation apparatus. The latter consists of a cylindrical cast iron kettle, standing upright, which is provided with consation domes and dephlegmators. The kettle must have a very high rising space, so that the oil vapors travel quite a long way in the kettle itself and thus find an opportunity to condense partially and to flow down over the superheated side walls, whereby they suffer a decomposition with the splitting-off of hydrocarbons with a lesser number of atoms of carbon, which are conducted off in vapor form and are condensed in the adjoining cooling device.

[fol. 1434] The chemical processes, which take place during cracking, may be explained by the help of the following considerations.

By the increase of temperature there are here caused reactions which take place with consumption of heat and can be considered as decomposition phenomena. The decomposition products are, however, for the greater part very unstable compounds, capable of reacting; therefore the decomposition reactions are followed by condensation phenomena of these dissociation products, in which complex bodies are produced. The latter decompose in their turn again; their decomposition products are again subjected to synthetic reactions and this goes on more or less often and more or less quickly the longer or the higher respectively the heating is applied.

The question rises, in which manner such decompositions and the synthetic reactions connected therewith take place?

It is probable that general, simple laws exist therefor, but these are not yet classified for high-boiling starting materials and one is limited to analogies with conditions which have been observed with low members of the hydrocarbon series.

In the first place there arises the question whether the decompositions are qualitatively dependent upon the temperature and are only influenced as to time by the height of the temperature or whether with increasing temperature there are produced qualitatively different decomposition products.

If what has just been said is applied to the pyrogenic decomposition of butane, it would have to be decided, whether there occurs always a decomposition in the sense of the equation

$$C_4H_{10} = CH_4 + C_3H_6$$

but at different temperature (600-1000° C) with increasing speed, or whether the splitting with increasing temperature would take place wholly or partly in the sense of another equation, f. e.

$$C_4H_{10} = C_2H_4 + C_2H_6$$

Concerning this important point there exists no complete certainty even in the case of the relatively well investigated hydrocarbons with few atoms of carbon.

Haber[1]) has ascertain that the reaction of splitting off of hydrogen stands in a characteristic connection with the [fol. 1435] temperature, in so far as at low temperatures, 600-800°, with aliphatic hydrocarbons there occurs only splitting of carbon chains, but elementary hydrogen is not split off, whereas this reaction is strongly noticeable from 900° up. The splitting of the hydrocarbon chains takes place in the same manner in the lower aliphatic members and only differs in time at the different temperatures, has been made probable by his investigations but not made certain.

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[1] (Habilitation volume, Karlsruhe 1895 (munich, R. Oldenbough).

4914

[fol. 1436]

EXHIBIT No. 400

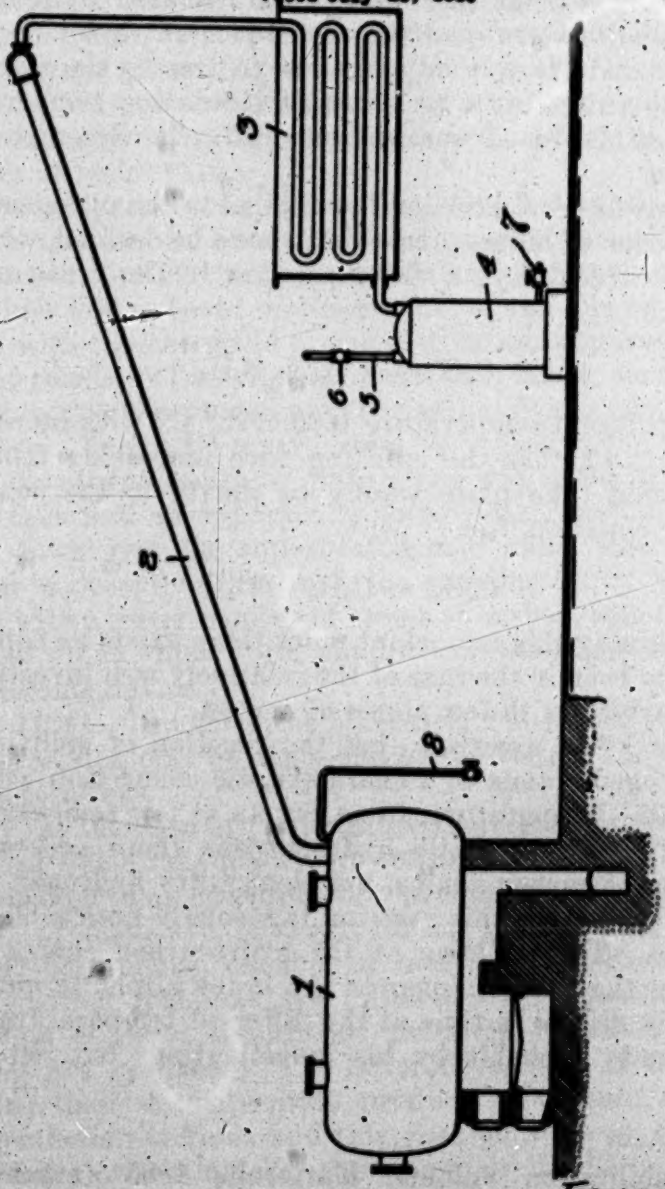
Sept. 15, 1925.

1,553,861

R. E. HUMPHREYS ET AL.

ART OF FORMING LOW BOILING POINT HYDROCARBONS

Filed July 21, 1919



Inventors.
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[fol. 1437] United States Patent Office

Patented Sept. 15, 1925. 1,553,861

Robert E. Humphreys, Francis M. Rogers, and Max G. Paulus, of Whiting, Indiana, Assignors to Standard Oil Company, of Chicago, Illinois, A Corporation of Indiana

Art of Forming Low-Boiling-Point Hydrocarbons

Application filed July 21, 1919. Serial No. 312,398

To all whom it may concern:

Be it known that Robert E. Humphreys, Francis M. Rogers, and Max G. Paulus, citizens of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in the Art of Forming Low-Boiling-Point Hydrocarbons, of which the following is a specification.

This process may be carried out in the apparatus diagrammatically illustrated in the accompanying drawing. In this apparatus 1 is a still; 2 a reflux fractionating condenser; 3 a final condenser preferably water cooled; 4 a receiving drum for distillate; and 5 a gas release pipe controlled by valve 6; 7 is a valved draw-off pipe for distillate. 8, a valved pipe through which samples of the vapors in the still can be withdrawn for test purposes.

The still is charged with a high-boiling-point hydrocarbon oil such as fuel-oil. Good success has been had with fuel-oil obtained from mid-continent petroleum having a Baumé gravity of 33.2 and having the following fractionation:

10% off at 478° F.;
20% off at 510° F.;
30% off at 532° F.;
40% off at 554° F.;
50% off at 576° F.;
60% off at 610° F.;
70% off at 632° F.;
80% off at 668° F.;
90% off at 712° F.;
98% off at 800° F.;

This charge is transformed into light products including naphtha having a maximum boiling point of 250° F. at rates

for naphtha formation of from 1.2 per cent per hour of the charge and upward by subjecting the charge under the conditions hereafter stated to continued temperatures of 740° F. and upwards, the rates of conversion varying in accordance with the temperatures as hereafter shown.

The foregoing naphtha fraction is selected for definite description because it forms a convenient index to the entire conversion process. Commercial gasolene (e. g. of a 400° F. maximum boiling point) may be considered as formed of a light fraction such as that with a maximum boiling point of 250° F. and a quantity of heavier material admixed therewith, the characteristics of the mixed product varying with commercial conditions and the purpose for which the product is to be used. In liquid phase pyrogenesis the various fractions seem to be formed in substantially constant relative proportions, and therefore any fraction such as the one here selected is a correct index of the performance of the process. In the practical manufacture of any desired commercial product (usually heavier than the naphtha of a main boiling point of 250° F.) this naphtha fraction will generally be taken off admixed with heavier fractions, and if, under the conditions chosen for the practice of the process, the product tends to come off heavier than desired, the undesired fractions will be removed from those desired either by reflux condensation or by subsequent fractionation of the distillate, and may be used as stock for further pyrogenesis.

The following table shows the formation rate of the naphtha fractions selected as an index of the process, and the formation rate of gasoline of a maximum boiling point of 400° F. at the various operating temperatures:

Mean temperature	740°	750°	760°	770°	780°	790°	800°	810°
Formation of naphtha at 250° F. maximum boiling point in per cent per hour.....	1.2	1.8	2.4	3.4	5.8	8.5	12	17
Formation rate of gasoline of 400° F. max. boiling point in per cent per hour.....	2.2	3.8	5.	7.5	12	17	24	35

The selection of the particular conversion rate will depend upon the choice of the op-rate-s. The lower conversion rates are mechanical construction of the apparatus and its ability to withstand the severe conditions prevailing at the higher conversion rates. The lower conversion rates are

readily attainable in a large size still without adopting unusual or unduly expensive methods of construction, whereas the higher conversion rates will, in many instances at least, require quite expensive apparatus per unit of capacity and the choice of operating conditions is therefore affected by the resultant of the two factors cutting in opposite directions, the lower unit cost of the apparatus making [fol. 1438] the lower conversion rates desirable while the increased running rates are used for the higher rates.

The above table shows the average results of actual runs wherein conditions were controlled as closely as is practicable, and shows a close approximation to results which may be attained in practice. Individual runs, however, may vary somewhat from these figures due to inevitable variations of conditions.

The conversion temperatures herein given are mean temperatures observed throughout actual runs. As a run progresses the stock gradually changes its composition in such a way that to maintain the vapor constitution in the vapor space within the still such that, with a given reflux condenser, the distillate will have a constant composition throughout the run, it is necessary either to lower the pressure or elevate the temperature slightly, and the common practice in commercial pyrogenesis leads us to prefer the latter expedient in running for distillate of a constant composition. The mean temperatures hereinbefore given are those of runs during which the temperature was thus somewhat raised.

During the conversion an atmosphere of which the vapor of the desired product constitutes approximately 4 per cent or upwards is maintained in the vapor space in the still. The conditions for maintaining this atmosphere can be determined for any given conversion rate by raising the still contents to the conversion temperature corresponding to that rate and then sampling the atmosphere. If the vapors of the desired finished product do not approximate 4 per cent or upwards then a higher concentration should be produced by raising the pressure upon the still until the proper atmosphere is obtained. The process can then proceed efficiently, it being assumed that the reflux condenser is sufficiently effective to give a final distillate in the receiving drum either of the desired constitution, or one in which the desired product is sufficiently high in percentage to

render it commercial to separate the undesired from the desired product by known methods of fractional distillation.

Purity of the final distillate can be enhanced either by increasing the reflux fractional condenser (as by increasing its size, improving its design or lowering its temperature) or by increasing the concentration of the vapors of the desired product in the vapor space in the still by still further raising the pressure.

It is essential to the production of commercial yields that gas which is constantly formed throughout the process be released from the still, as through the pipe provided for the purpose. Since this gas carries vapors of the desired final products it should be thoroughly cooled as in the condenser shown before being released. It is usually desirable to permit to pass over into the final condenser, in addition to the gas and vapor necessarily carried therewith, a very considerable quantity of vapors of the desired product, but the extent to which these pass over, contemporaneously with the conversion, is a matter which may be considerably varied at the option of the operator. If the reflux fractionating condenser be made of large capacity and the vapors of the desired fractions be highly concentrated in the vapor space in the still, then it is possible to maintain a high percentage of the reaction product in the still during the period of conversion. If the reflux fractionating condenser be of small capacity or be entirely omitted, a high percentage of the conversion product will pass over during the conversion while if the concentration of vapor of the desired product in the vapor space of the still approximates the minimum above stated then the bulk of the conversion products will pass over as rapidly as they are formed.

While we have stated the rates of conversion to be anticipated with a particular charging stock, we have found that variations in the stock, while producing quite noticeable variation in rates, are relatively unimportant as compared with the temperature variations readily controllable by the operator, a change in temperature to the extent of a relatively few degrees being sufficient to produce these rates with any charging stocks which it is believed are likely to be commercially available.

This process results in rapidly and efficiently producing the desired products, its especial advantage being the pre-

dictable nature of the resulting product arising from the fact that, knowing the conversion rate the operator can readily vary conditions to produce whatever particular results he desires. Generally speaking this process is economical of fuel, and in most variants of the process the fuel economy is very high.

The extent to which the process is carried depends upon practical conditions. In any process generically like the present there is a tendency for coke to form slowly on the bottom and this tends to produce hot bottoms with danger of accident. Fifty per cent at least of the contents of the still can be safely transformed under normal conditions and in test runs, sometimes as high as seventy per cent, can be transformed, but, in general, carrying of the conversion to so high a point produces hot bottoms with too great frequency to be safe in commercial practice in any large size still. In a small size still, where the surface to volume relation is greater, the coke forms in a thinner layer and the still can also be conveniently made much stronger and [fol. 1439] it may be possible with small stills to carry the conversion to a very considerable extent. There will usually be left a residue in the still. This residue contains a small percentage of suspended solid or semi-solid matter and is not suitable for use as charging stock as it is drawn off, but the major part of it is closely similar to the original charging stock and it may be rerun at atmospheric pressure to coke or to a heavy residue and the distillate can then, if desired, be utilized as charging stock for a second operation.

What we claim as new and desire to secure by Letters Patent is:

1. The herein described improvement in the art of liquid phase pyrogenesis of high-boiling point petroleum fractions consisting in treating a body of liquid petroleum in a closed receptacle, maintaining in the vapor space above the liquid an atmosphere containing approximately 4 per cent or upwards of vapors of a desired finished product having a maximum boiling point between 250 and approximately 400° F. by exerting pressure upon the receptacle, causing the conversion of portions of the body of liquid petroleum into naphtha fractions boiling at and below 250° F. at conversion rates of from 1.2 per cent per hour of the volume of the charge to 17.7 per cent hour of the volume of the

charge by maintaining the liquid body at the herein described conversion temperatures of from 740° F. to 810° F., the temperature for any given rate within said range being as herein set forth, removing from the receptacle gas generated in the conversion and cooling the gas to condense from it the vapors of the desired product.

2. The process of claim 1 characterized by the fact that contemporaneously with the conversion a high percentage of the desired product is distilled out of the receptacle.

3. The herein described improvement in the art of liquid phase pyrogenesis of high-boiling point petroleum fractions consisting in treating a body of liquid petroleum in a closed receptacle, maintaining in the vapor space above the liquid an atmosphere containing approximately 4 per cent or upwards of vapors of a desired finished product having a maximum boiling point between 250 and approximately 400° F. by exerting pressure upon the receptacle, causing the conversion of portions of the body of liquid petroleum into naphtha fractions boiling at and below 250° F. at conversion rates of from 1.2 per cent per hour of the volume of the charge to 17.7 per cent per hour of the volume of the charge by maintaining the liquid body at the herein described conversion temperatures of from 740° F. to 810° F., the temperature for any given rate within said range being as herein set forth, removing from the receptacle gas generated in the conversion, and subjecting the vapors passed out of the receptacle to the action of a reflux fractionating condenser to return to the still for further pyrogenesis the fractions heavier than the desired product.

4. The herein described improvement in the art of liquid phase pyrogenesis of high-boiling point petroleum fractions consisting in treating a body of liquid petroleum in a closed receptacle, maintaining in the vapor space above the liquid an atmosphere containing approximately 4 per cent or upwards of vapors of a desired finished product having a maximum boiling point of 400° F. by exerting pressure upon the receptacle, causing the conversion of portions of the body of liquid petroleum into fractions boiling as low as 400° F. at conversion rates of from 2.2 per cent per hour of the volume of the charge to 35 per cent per hour of the volume of the charge by maintaining the liquid body at the

herein described conversion temperatures of from 740° F. to 810° F., the temperature for any given rate within said range being as herein set forth, removing from the receptacle gas generated in the conversion and cooling the gas to condense from it the vapors of the desired product.

Robert E. Humphreys, Francis M. Rogers, Max G. Paulus.

[fol. 1440] Exhibit No. 401 appears on page 465 of the Master's Report.

[fol. 1441] EXHIBIT No. 402

R. L. HUMPHREYS.
PETROLEUM DISTILLING APPARATUS.
APPLICATION FILED JUNE 14, 1913.

1,122,002. Patented Dec. 22, 1914.

Fig. 2

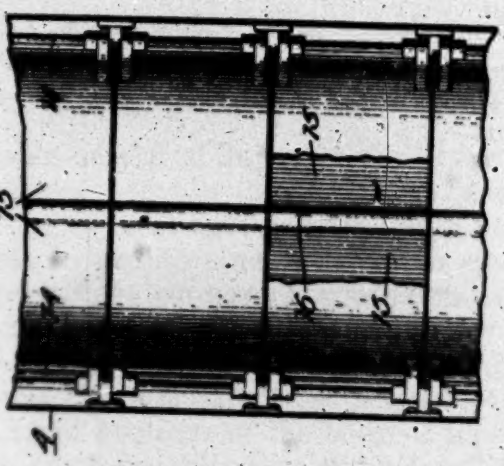
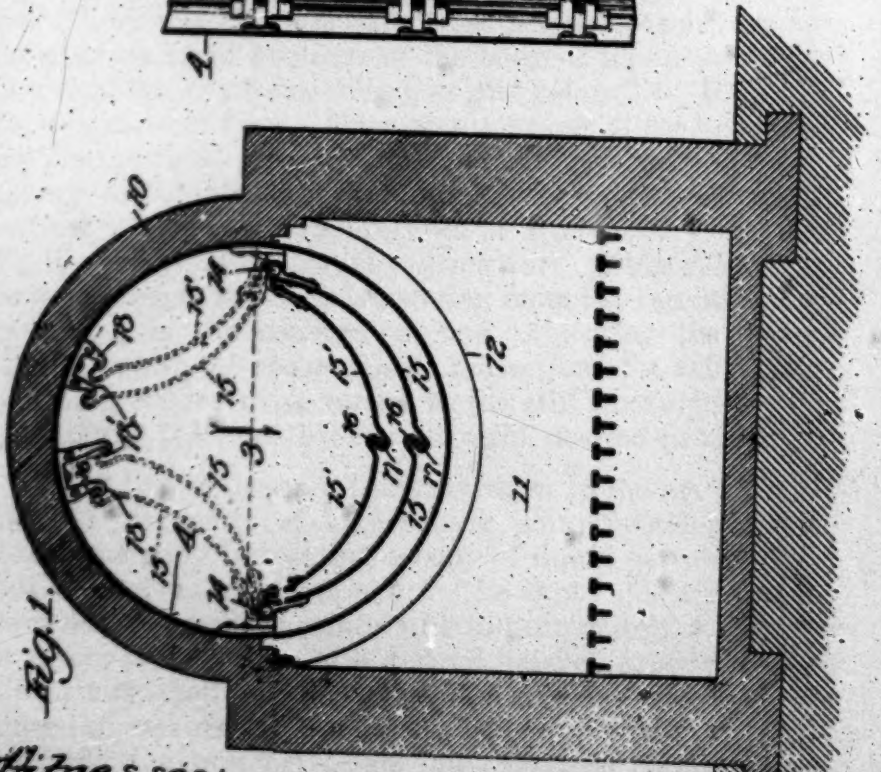


Fig. 1.



Witnesses:

Inventor.
Robert L. Humphreys,
By Dyer, Brittain, Chester & Hale
Attys.

[fol. 1442] United States Patent Office

Robert E. Humphreys, of Whiting, Indiana, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana.

Petroleum-Distilling Apparatus

1,122,002. Specification of Letters Patent. Patented Dec. 22, 1914

Application filed June 14, 1913. Serial No. 773,750

To all whom it may concern:

Be it known that I, Robert E. Humphreys, a citizen of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in Petroleum-Distilling Apparatus, of which the following is a specification.

My invention relates to an improvement in the still of petroleum-distilling apparatus, which I have devised, more immediately, for the apparatus employed in practising the process of manufacturing gasolene set forth in United States Letters Patent No. 1,049,667, granted January 7, 1913, to W. M. Burton.

In commercially practising the aforesaid process on a large scale, wherein the capacity of the still and the quantity of the material treated therein is several thousand gallons, it is found that the accumulation of carbon on the still bottom precludes conducting the run long enough to convert into gasolene more than about one-third of the material contained in the still. This is because the carbon, being a good insulator of heat, becomes red hot and if the run were continued, would soon burn through the bottom of the still, besides tending to retard the progress of distillation.

The primary object of my invention is to prolong the run to an extent that will enable, say, two-thirds, more or less, of the still-contents to be converted into gasolene without incurring the objectionable consequences referred to, and this I accomplish by the means illustrated in the accompanying drawing, in which—

Figure 1 is a transverse section through a still provided with my improvement, and Fig. 2 is a plan section of a broken portion of the same on line 3, Fig. 1.

In the still, 4, and preferably along diametrically-opposite points therein, extend pintle-rods 14, 14, reaching approximately to the ends of its cylindrical section. On these opposite rods are hinged, at their outer ends, concavo-convex plate-sections 15 to form a series thereof along each rod, opposite sections, or members of the series, releasably interlocking at their inner ends, as by means of a hooked edge 16 formed along each section of one series and a hooked edge 17 along each section of the other series, to form a plate covering, and conforming at least approximately to the curved shape of, the still-bottom; although the curved shape of the sections is not an essential feature of my invention. These sections 15 may mutually overlap each other, lengthwise of the still, at their meeting edges, or be there more or less slightly separated, as represented in Fig. 3; but they should interfit more or less loosely, and there is ample space about their outer hinged edges to permit the liquid contents of the still to circulate freely therein, in boiling, in contact with the upper and lower plate-surfaces. Hooks 18 are shown to depend in two series inside the still along the central portion of its top to engage the hooks on the respective sections when they are raised, and hold them up when it is desired to clean out, from the still, any accumulation of free carbon beneath them. It is desirable to provide at least two sets of these plates, and a second set is shown suspended to extend over the lower set already described, and is formed, like the latter, of interlocking sections 15′, these sections being hinged along their outer edges on the pintles 14 in a manner to alternate their hinge-knuckles with those of the lower set, and being adapted to be held in their raised positions by hooks 18′.

In the operation of the still, the liquid-hydrocarbon contents being boiled by the heat from the furnace, circulate freely about the plates and over their upper and lower surfaces, upon which the carbon, produced by the aforesaid reaction, forms for the most part, and in comparatively small quantity, producing a mere film. The primary purpose of forming the plates of adjustable sections is to adapt

them to be raised out of the way to permit access to the lowermost for removing the carbon formed upon it after removing that which has similarly formed on the upper plate, and to permit access to the bottom of the still for the same purpose. After a run of the apparatus, or when the accumulations of carbon render it desirable, the still is opened and the carbon formed on the top surface of the upper plate is brushed off and taken out through the manhole, whereupon the sections 15′ are raised and locked in the raised position, and the bottom surfaces of the raised sections and top-surface of the lower plate are cleaned; then the sections 15′ are raised and their lower surfaces are [fol. 1443] cleaned in the same way, and access to the still-bottom is thus afforded for removing from it the relatively-small quantity of carbon formed thereon.

I realize that considerable variation is possible in the details of construction thus specifically shown and described, and I do not intend by illustrating a single, specific or preferred embodiment of my invention to be limited thereto; my intention being in the following claims to claim protection upon all the novelty there may be in my invention as broadly as the state of the art will permit.

What I claim as new and desire to secure by Letters Patent is—

1. In an apparatus of the character described, the combination with a still, of a plurality of plates extending therein one over the other and spaced apart and from the still-bottom, said plates forming spaces for the circulation about and over them of the still-contents undergoing distillation.

2. In an apparatus of the character described, the combination with a still, of adjustable plate-forming sections extending therein over and spaced from the still-bottom, and forming spaces for the circulation about and over them of the still-contents undergoing distillation.

3. In an apparatus of the character described, the combination with a still, of a plate extending therein over and spaced from the still-bottom and comprising sections hinged in the still to its opposite sides to meet at their inner edges and provided with releasable means for interlocking them in their meeting position.

4. In an apparatus of the character described, the combination with a still, of a plate extending therein over and spaced from the still-bottom, and comprising series of sections hinged at their outer edges in the still to its opposite sides to meet at their inner edges, and provided on said inner edges with hooks for releasably interlocking them in their meeting position.

5. In an apparatus of the character described, the combination with a still, of pintles extending along its opposite inner sides, curved plate-sections having knuckles on their outer edges at which they are hinged on the pintles and adapted to meet at their inner edges in their plate-forming relation, hooks on the inner edges of said sections for releasably locking them in said relation, and hooks depending in the still from its top-portion in position to engage with the hooks on said sections to hold them when raised.

Robert E. Humphreys.

In presence of L. Heislar, A. C. Fischer.

[fol. 1444] Exhibit No. 405 appears in page 470 of the Master's Report.

[fol. 1445]

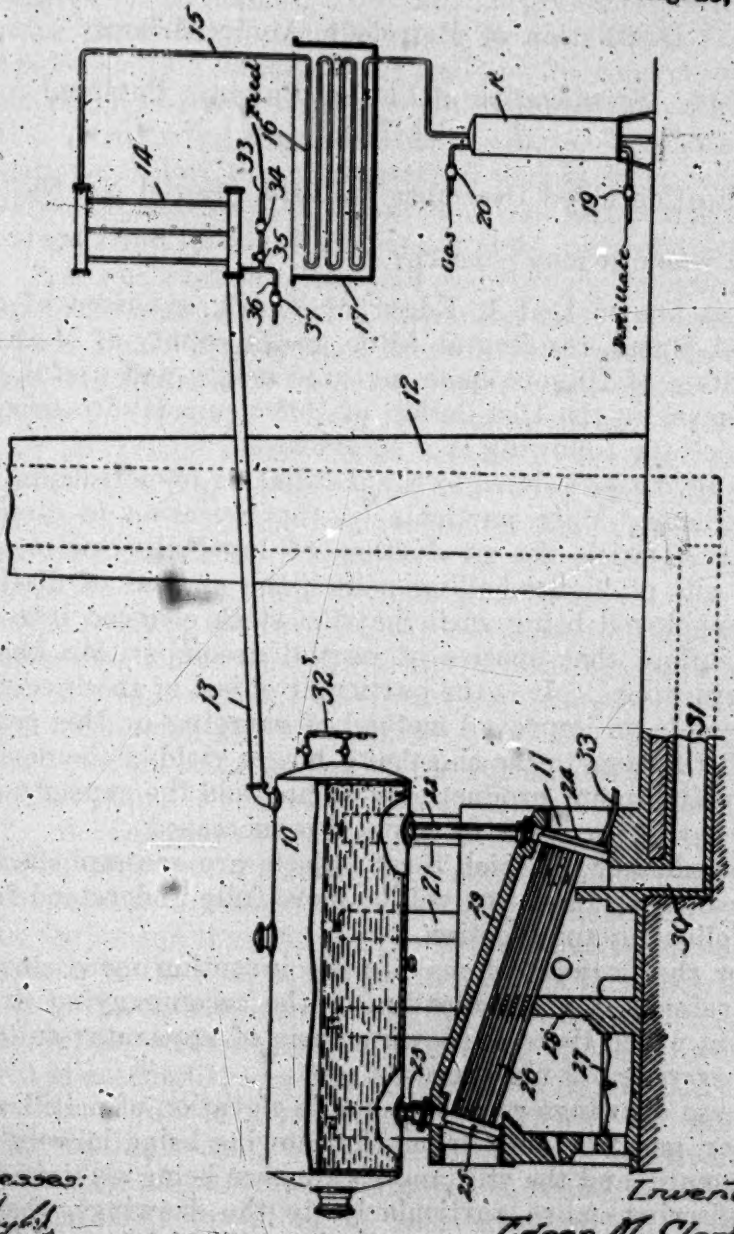
EXHIBIT NO. 407

E. M. CLARK.

DISTILLATION OF PETROLEUM HYDROCARBONS.

APPLICATION FILED DEC. 14, 1915.

1,388,514. Patented Aug. 23, 1921.



Witnesses:

Inventor:

Edgar M. Clark.

[fol. 1446] United States Patent Office

Edgar M. Clark, of Alton, Illinois, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Distillation of Petroleum Hydrocarbons

1,388,514. Specification of Letters Patent. Patented Aug. 23, 1921

Application Filed December 14, 1915. Serial No. 66,702

To all whom it may concern:

Be it known that I, Edgar M. Clark, a citizen of the United States, residing at Alton, in the county of Madison and State of Illinois, have invented a new and useful Improvement in the Distillation of Petroleum Hydrocarbons, of which the following is a specification.

My invention relates to the distillation of petroleum hydrocarbons. More particularly, the invention is directly concerned with the production of low-boiling-point oils from oils of higher-boiling points, the method of distillation employed being such that the stock charged into the still suffers that species of partial decomposition known as "cracking." It is the particular object of the invention to provide an improved method of carrying on this cracking distillation, to the end that a larger yield of the desired low-boiling-point product may be had and the capacity and efficiency of the cracking apparatus increased.

The manner in which these objects are accomplished by the use of my invention will be more fully understood from the following specification.

For the purpose of making my invention more clear, I will refer in the specification to the accompanying drawings in which there is shown a form of apparatus suitable for carrying out my process.

These drawings represent a side elevation of a still, condenser, and receiving drum, the showing being largely diagrammatic and the still and its furnace being sectioned.

Referring, more particularly, to the drawings, the numeral 10 designates, in general, the still which is used in my process. A furnace 11 is used for heating this still, the flue

gases from the furnace escaping through a stack 12. The vapors rising from the still are carried off by an upwardly inclined vapor pipe 13, known as a run-back or dephlegmator. At the upper end of this dephlegmator is mounted a fractional condenser 14 so arranged that its condensate returns to the dephlegmator and traverses the latter to reenter the still. From the upper portion of the fractional condenser 14 a vapor line 15 leads to the condenser proper 16, which is shown as a pipe coil mounted in a water bath 17. A receiving drum for the distillate, designated 18, is mounted below the condenser 16 and is provided with a valved liquid draw-off 19 and a valved gas-escape pipe 20, valved from its lower and upper ends, respectively.

The construction of the still and furnace designated generally 10 and 11 is shown in section in the drawing from which it will be seen that the still body which is of horizontal cylindrical form is supported upon colums 21 to lie above the furnace. From the shell or drum of the still, a pair of vertical trunks 22, 23, located at the rear and front of the shell respectively, lead downward and into the furnace proper. At the lower ends of these trunks are connected headers 24, 25, between which extends a bank of tubes 26. These tubes are heated as by a grate 27, located in the front of the furnace, the hot gases of combustion being compelled to pass upwardly through the bank of tubes by the bridge wall 28, which extends through the tube bank and terminates just short of the crown 29. Leading downwardly from the rear end of the furnace is a vertical conduit 30 which is connected by the passage 31 with the stack 12. A gage glass 32 is applied to the rear end of the still.

The still and furnace construction above described is particularly desirable for operating under high pressure for the reason that the shell or drum itself is not subjected directly to the heat of the furnace and is therefore not subject to the development of hot spots with their accompanying danger of explosion. The heating of the oil within the still is accomplished solely by the tubes 26 which, as shown, are arranged at a considerable angle to the horizontal whereby the heating of the oil results in a relatively rapid or forcible thermo-siphon circulation, which is sufficient to prevent the deposition of suspended carbon within the

tubes themselves. A drain pipe 33 is tapped into the lower end of the header 25, that being the lowest point in the still.

The apparatus above described is particularly designed for use in carrying out the process of producing low-boiling-point hydrocarbons from hydrocarbons of higher boiling points, as broadly defined in the patent of William M. Burton, No. 1,049,667, and my own prior Patent No. 1,119,496.

In carrying out this process by the use of the apparatus I have just described, the high-boiling-point stock which it is desired to convert into oil of a lower boiling-point is in- [fol. 1447] troduced in the still 10 and is heated by means of the furnace 11.

As in the case of the Burton process referred to, the still, dephlegmator, and condenser form a single system the parts of which are in free communication. In the distillation process, therefore, the vapors generated in the still pass freely therefrom and to and through the condenser. From the latter the distillate and any uncondensed gases pass into the receiving drum, and the distillate there collects to be drawn off either continuously or intermittently by the draw-off pipe 19, while the gases are permitted to discharge through the valved pipe 20. By controlling the escape of these uncondensed gases, the entire system, including the still, may be brought up to any desired pressure and, the temperature of the still being proportionately raised, distillation may be continued under this pressure. Such is the general operation of the apparatus as so far described.

It is found in practice that when working with a stock of petroleum hydrocarbons composed of fractions having boiling points ranging upwardly from 400° F. or thereabout, the distillation pressure being about 7 atmospheres and the temperature from 650 to 850° F. or thereabout, the character of the reactions taking place is such that the last 25 to 35 per cent. of the still charge is exceedingly refractory; in fact, it is considered uneconomical in large plants to further continue the distillation when the charge has been reduced to this volume. When this point has been reached therefore, it is common to draw the furnace fires, drain, clean and inspect the still, and then re-charge with a fresh stock bringing this stock up to heat and distilling

as before until about 65 to 75 per cent has gone over, at which point the run is said to be finished.

It is the particular object of my invention to improve the process above defined to the end that the output of distillate at each run of the still may be considerably increased. I find that this may be accomplished by feeding either continuously or intermittently during the progress of the distilling operation a regulated quantity of fresh stock. I have found that under proper conditions I may add to the still during the run of the latter upward of 200 per cent of the normal charge of the still and this without increasing proportionately the length of time required to complete the run. By my improved process, therefore, both the capacity and the efficiency of the apparatus is measurably increased.

I find that the best results are obtained when the additional stock is charged into the upper end of the dephlegmator 13 and is permitted to traverse the length of the latter before reaching the still. In the drawings I have shown a supply pipe 33 for introducing this additional charge, the pipe being provided with a cut-off valve or regulating valve 34 and a check valve 35. The pipe 33 will be connected with a supply of oil under pressure and by regulating this pressure or by regulating the valve 34 the feed may be nicely adjusted to give the best results. I have shown a drain pipe 36 provided with a valve 37 tapped into the pipe 33, the drain pipe being adapted to draw off any tar which may collect at the foot of the air condenser 14 at the end of a run, or during the run.

In distilling petroleum hydrocarbons according to my process therefore, the following procedure will be employed:

The still 10 will be charged with the stock to be converted, the charge being sufficient to fill the still with the exception of a small vapor space at the upper surface of the liquid in the shell or drum. Fuel oil, gas oil, or the like residues boiling well above 400° F. and, in the instances mentioned, above 500° F. are the common stocks now employed by me. The furnace 11 being fired the still will be brought up to its operating temperature. The gas escape pipe 20 will preferably be left open during the initial heating of the still so that any small quantity of water or low boiling point material in the stock may be driven off freely.

As the temperature of the still approaches the boiling point of the stock, the gas valve of the pipe 20 will be closed, and the pressure will then rise slowly, due to the formation or liberation of small quantities of incondensable gases, or the fact that the condenser does not act to condense the vapors as fast as they are produced. In this connection it should be noted that in place of permitting the still to build up its own internal pressure, it is preferable to supply inert incondensable gas under pressure from an external source, as from another still which is in normal operation. This method of operation is described more fully in my prior Patent No. 1,129,034.

The internal pressure of the still and its connected dephlegmator and condenser having reached the desired point, for instance from 4 to 7 atmospheres or upward, the gas valve is properly regulated to maintain this pressure and as the temperature of the still rises under continued firing, the distillation and cracking commence, as evidenced by the flow of the desired low-boiling-point products (i.e., crude gasolene) into the receiver from the condenser.

When this condition has been reached, the run is proceeded with until the liquid line in the still shows in the gage glass, and the temperature of the still contents has been appreciably increased. The feed of additional stock may now be commenced, the valve 34 being opened for this [fol. 1448] purpose. The rate of feed should be such as to maintain a fairly uniform liquid level within the still, as indicated by the gage glass. The fresh stock will therefore be supplied at about the rate of the collection of distillate in the receiver, although this figure is approximate only. As the distillation proceeds, the stock in the still remains about constant as to volume, but gradually becomes more refractory, and requires much higher temperatures for "cracking." After upward of 200 per cent of the original charge has been fed into the still, the liquid body in the still has become so heavy, and the temperatures for "cracking" so high, and the proportion of fuel required to maintain these temperatures to distillate produced so great, that it is considered more economical to terminate the run than to continue. The valve 34 is therefore closed, the drain valve 37 opened, the fires drawn, and the still drained through the pipe 33, preparatory to cleaning and inspection.

By feeding the additional stock into the top of the dephlegmator instead of directly into the still a highly important operative advantage is obtained in that the fresh stock is thoroughly freed of any contained moistures, and in fact is fractionated and subjected to some cracking before reaching the still proper. The disadvantages and dangers of introducing raw stock into a highly heated still are thereby completely obviated.

In the foregoing specification I have set forth in considerable detail one method of carrying out my new process, and have also described the general arrangement and construction of one form of apparatus which I find suitable for use in the commercial operation of the same. It is to be understood, however, that these details are illustrative only and for the purpose of making the invention more clear, and that I do not regard my invention as limited in any sense to these illustrated details, except in so far as I have included such limitations within the terms of the appended claims in which it is my intention to claim all novelty inherent in my invention as broadly as is possible in view of the prior art.

What I claim as new and desire to secure by Letters Patent is:

1. The process of treating petroleum hydrocarbons of relatively high boiling points to produce therefrom hydrocarbons of lower boiling point which consists in distilling a liquid body of such high-boiling-point stock under a pressure sufficient to effect its decomposition, carrying off the vapors of distillation while under the said pressure through a suitable unheated conduit leading away from the still, introducing fresh stock into the said conduit and causing it to traverse the latter and enter the still therethrough, and condensing and collecting the said vapors.

2. The process of treating residual petroleum hydrocarbons of the character of gas oil or fuel oil, to produce therefrom gasolene hydrocarbons, which process consists in distilling a liquid body of such residual hydrocarbons under a pressure sufficient to effect its decomposition, carrying off the vapors of distillation while under the said pressure through a suitable unheated conduit leading away from the still, introducing a fresh supply of said residual hydrocarbons into the said conduit and causing it to traverse the lat-

ter and enter the still therethrough, and condensing and collecting the said vapors.

3. The process of treating petroleum hydrocarbons of relatively high boiling points to produce therefrom hydrocarbons of lower boiling point, which consists in distilling a liquid body of such high-boiling-point stock under a pressure sufficient to effect its decomposition, carrying off the vapors of distillation while under the said pressure through a suitable unheated conduit leading away from the still, condensing and collecting the said vapors, and introducing a fresh stock into the said conduit, the total quantity of additional stock so introduced being less than the quantity of distillates, and causing said fresh stock to traverse the said conduit and enter the still therethrough.

4. The process of treating petroleum hydrocarbons having a boiling point of upwards of 450° F. at atmospheric pressure, to produce therefrom hydrocarbons of the gasolene series, which consists in distilling a liquid body of such high-boiling-point stock under a pressure of upward of 4 atmospheres, carrying off the vapors of distillation while under the said pressure through a suitable unheated conduit leading away from the still, introducing fresh stock into the said conduit and causing it to traverse the latter and enter the still therethrough, and condensing and collecting the said vapors.

Edgar M. Clark.

In presence of Seymour Anderson, Wm. G. McCullam.

[fol. 1449] EXHIBIT No. 408

G. CASH.
STUFFING BOX.
APPLICATION FILED DEC. 14, 1916.

1,230,065. Patented June 12, 1917.

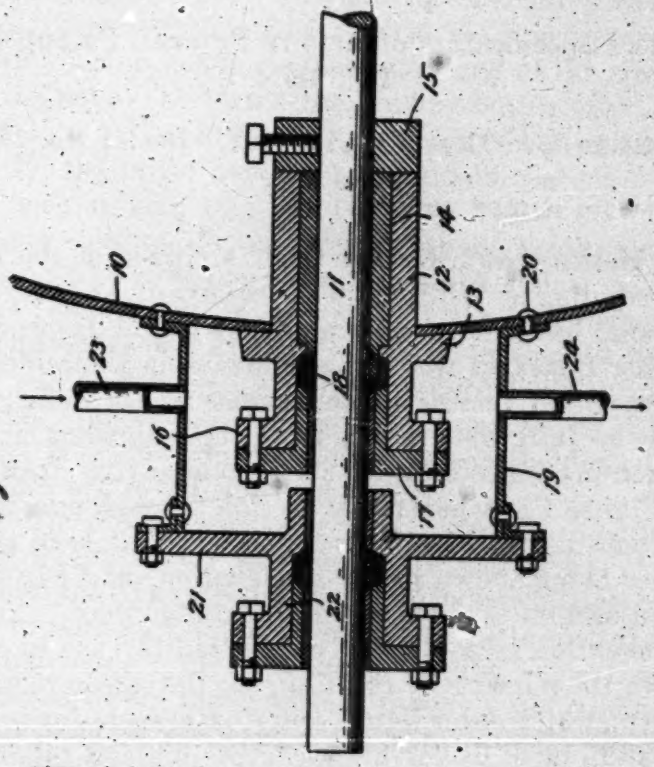


Fig. 2.

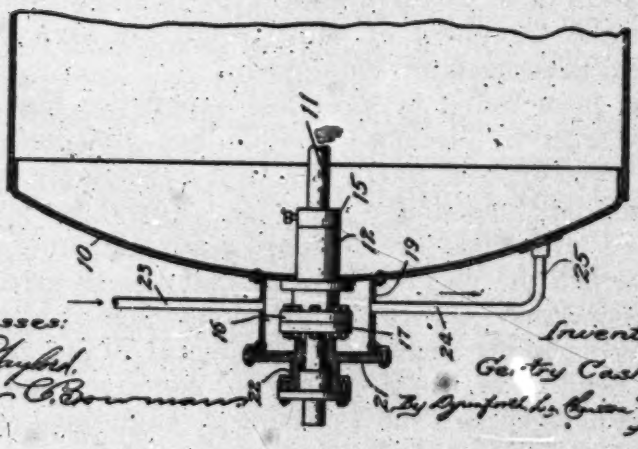


Fig. 1.

Witnesses:
Chas. Clayfield.
Jno. C. Bowman.

Inventor:
Gentry Cash.
By Bakewell & Byron & Whittemore
Attys.

[fol. 1450] United States Patent Office

Gentry Cash, of Whiting, Indiana, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Stuffing-Box

1,230,065. Specification of Letters Patent. Patented June 12, 1917

Application filed December 14, 1916. Serial No. 137,043

To all whom it may concern:

Be it known that I, Gentry Cash, a citizen of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in Stuffing-Boxes, of which the following is a specification.

My invention relates to improvements in stuffing-boxes and will be fully understood from the following specification taken in connection with the accompanying drawing, in which Figure 1 is a horizontal section through one end of a liquid container to which my stuffing-box has been applied, the latter being shown partly in elevation; and Fig. 2 is an enlarged section taken through the stuffing-box.

My invention is particularly designed for use in connection with the packing of rotating, oscillating or reciprocating shafts, which enter liquid containers, such, for instance, as digesters or stills for hydrocarbon oils and other materials in the treatment of which relatively high temperatures and pressures are employed.

It has been found by practical experience that the ordinary forms of stuffing-boxes do not give satisfactory service when exposed to the effects of exceedingly hot gases or liquids confined under pressure. For these particular services I have therefore designed a novel form of stuffing-box in which the packing joint or gland is so arranged as to give good service with a minimum amount of attention.

Referring to the drawing, the numeral 10 designates the convex head or end of a cylindrical container and the numeral 11 designates a shaft passing through this head. The stuffing-box for the shaft is of compound form, being, in

fact, made up of two stuffing-boxes arranged in tandem. The inner stuffing-box comprises a sleeve 12 having a collar 13 formed integrally thereon intermediate its length and welded or otherwise secured hermetically to the container-head 10. The sleeve 12 may be lined with a bearing-bushing 14 for supporting the shaft 11, the latter being shown as secured in position by a collar 15 detachably fastened thereto and normally abutting against the inner end of the sleeve and bearing-bushing. The outer end of the sleeve 12 beyond the collar 13 forms the stuffing-box proper, being provided with a flanged head 16 to which is bolted a gland-member 17, the latter serving to retain in place the usual annular packing-ring 18.

The inner stuffing-box made up of the sleeve 12, gland 17 and packing-ring 18 is housed within a cylindrical casing 19 riveted to the head 10, as shown at 20, the joint being gas-tight. The outer end of the cylindrical casing 19 has detachably secured thereto a cover-casting 21 which carries the second stuffing-box generally designated by 22 and which may be of the construction shown in the drawing, or of any other approved construction.

The intermediate chamber or jacket-space formed by the casing 19 is preferably provided with means by which a cooling fluid may be introduced and withdrawn, such means comprising inlet and outlet pipes 23 and 24 tapped into the wall of the casing. This system of cooling is particularly advantageous where the container to which the stuffing-box is applied is to be constantly fed with a fresh supply of liquid. Under such conditions the outlet-pipe 24 may be led from the jacket or casing 19 directly into the container, as shown at 25 in Fig. 1 of the drawing.

By the construction above described the inner stuffing-box may be kept cool by the constant flow of a cooling liquid through the housing-chamber or jacket surrounding the same, and by this means the destructive effect of the high temperature existing within the container is avoided. Furthermore, the pressure within the jacket surrounding the outer end of the inner stuffing-box may be kept at approximately the same figure as that existing within the container, and the pressures on the two sides of the stuffing-box being substantially the same, leakage through the box is reduced to a minimum. It is true that under these condi-

tions the outer stuffing-box 22 will be subjected to the high pressure of the jacket-space but such high pressure will not be accompanied by high temperature and the destructive effect on the packing of the outer box is therefore far less. In addition it will be noted that a relatively valueless liquid may be employed for cooling, and the leakage of such liquid through the outer stuffing-box would represent no great loss.

The greatest advantages may be obtained from my in- [fol. 1451] vention, however, where it is possible to feed liquid into the container through the intermediate jacket of the stuffing box. Under such circumstances no attention need be paid to slight deterioration and leakage of the inner stuffing-box. The pressure in the jacket being greater than the pressure within the container any flow of liquid through the inner stuffing-box will be inward and not outward and the stuffing-box itself will act as an inlet, supplementing the pipe 25.

By the use of my invention I find it possible to adequately pack and keep packed shafts entering oil sills and digesters where the temperature and pressure conditions are such that no satisfactory results may be had with any other form of stuffing-box known to me.

While I have shown and described in considerable detail one specific embodiment of my invention, and have set forth some of the advantages of my invention in certain specific uses, it is to be understood that this showing and description is illustrative only and for the purpose of making my invention more clear, and that I do not regard the invention as limited to these details, nor to any of them, except in so far as such limitations are included within the terms of the accompanying claims in which it is my intention to claim novelty inherent in my invention as broadly as is permissible in view of the prior art.

What I claim as new and desire to secure by Letters Patent is—

1. In combination, a container, a stuffing-box extending to the outside of said container, and means for supplying a liquid medium to the container said liquid serving as a cooling medium for the stuffing-box.

2. In combination, a container, a stuffing-box extending to the outside of said container, a housing inclosing the

outer end of said stuffing-box, and means for supplying a liquid medium to the container said liquid serving as a cooling medium for the stuffing-box.

3. In combination a container, a shaft entering the same, a stuffing-box forming a joint between the said container and shaft, a housing inclosing the outer end of the said stuffing-box, a second stuffing-box forming a joint between said housing and said shaft, and means for introducing fluid into the said container through the chamber formed by the said housing.

Gentry Cash.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents, Washington, D. C."

[fol. 1452] EXHIBIT No. 409

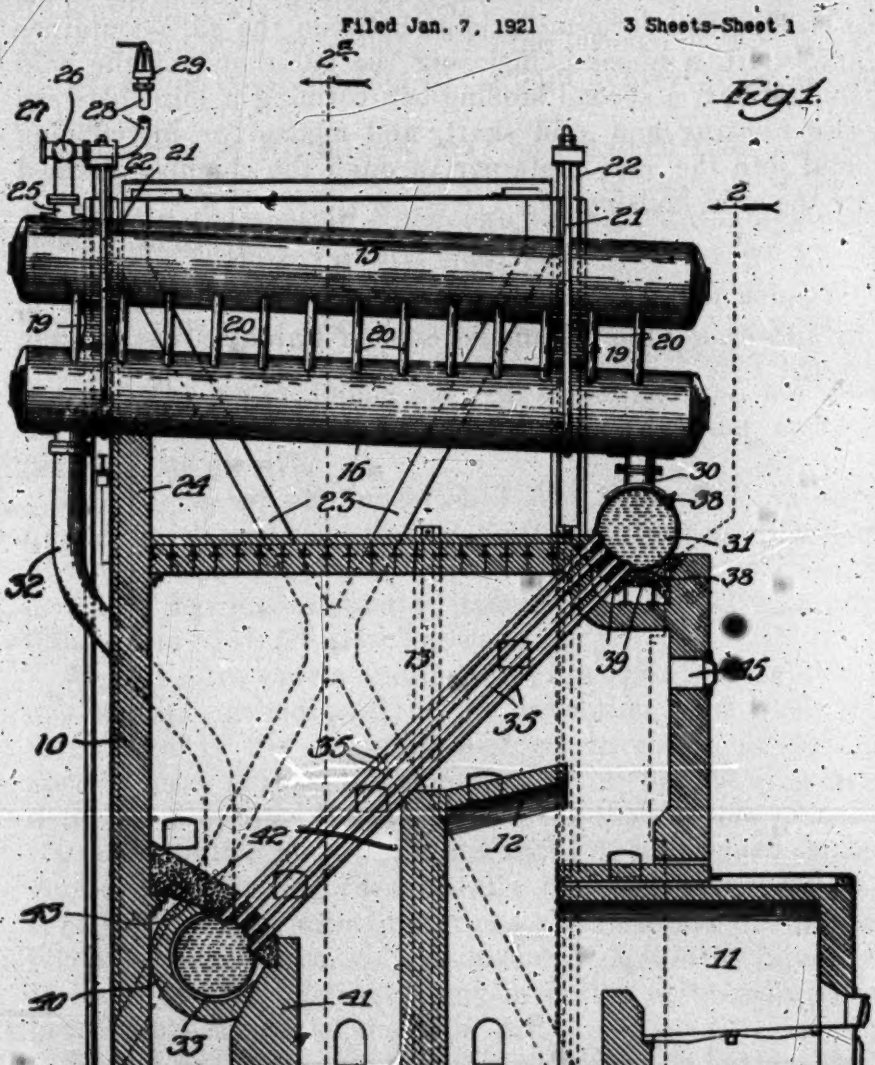
May 4, 1926. 1,582,929

R. E. HUMPHREYS

PRESSURE OIL STILL

Filed Jan. 7, 1921 3 Sheets-Sheet 1

Fig. 1.



Inventor:
Robert E. Humphreys,
By Dyer, Brown, Duell, Chittim & Hale,
Attys.

[fol. 1453]

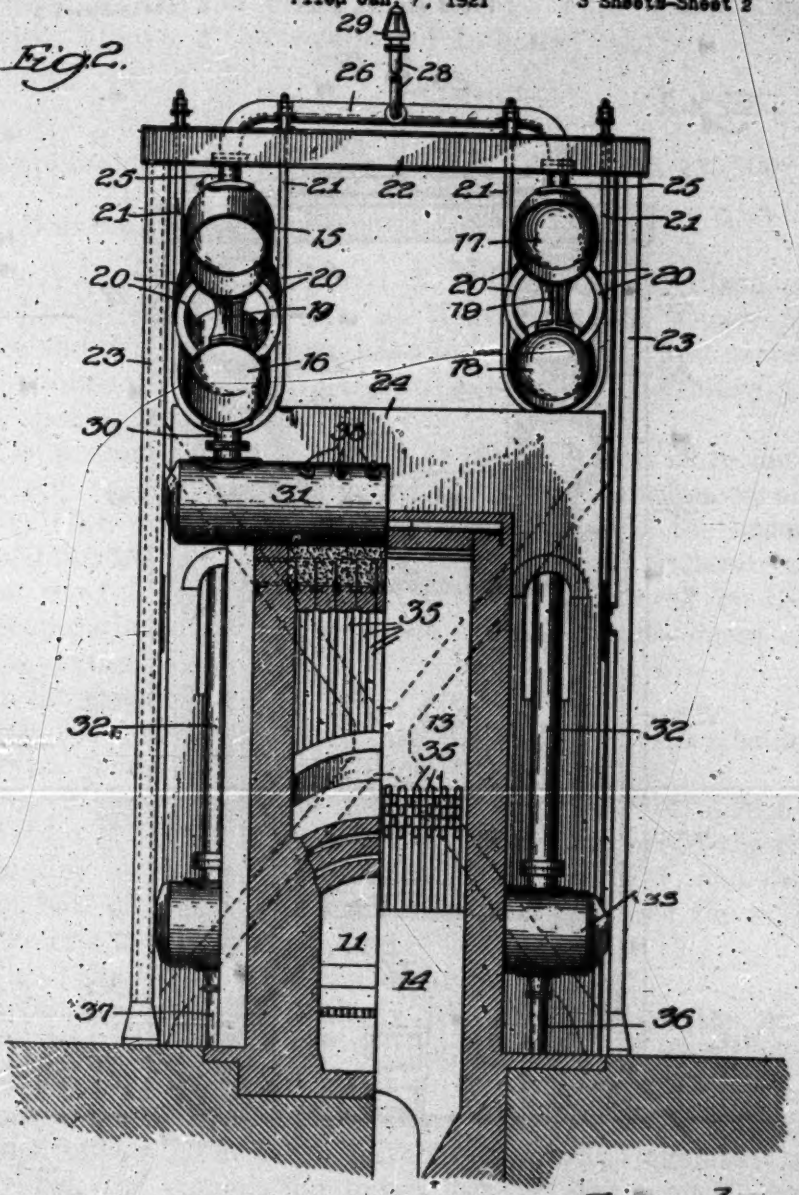
May 4, 1926. 1,582,929

R. E. HUMPHREYS

PRESSURE OIL STILL

Filed Jan. 7, 1921 3 Sheets-Sheet 2

Fig 2.



Inventors:
Robert E. Humphreys,
By Dyrenforth, Lee, Chritton & Wiley
Attys.

4942

[fol. 1454]

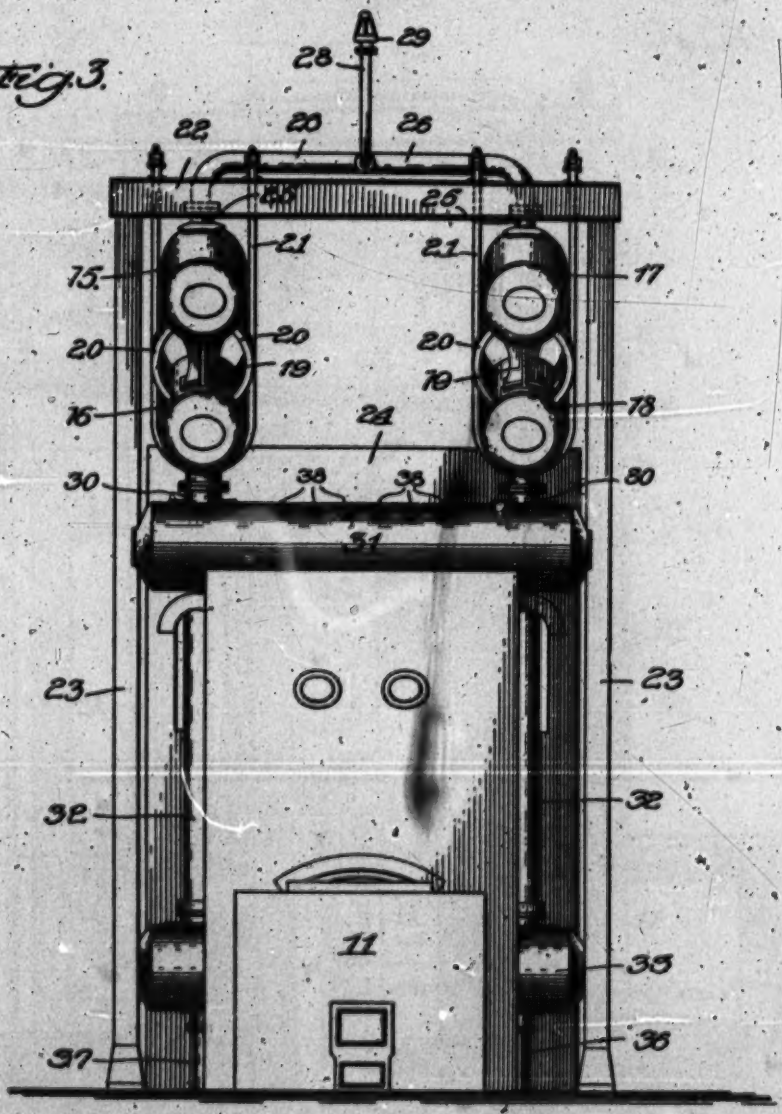
May 4, 1926. 1,582,929

R. E. HUMPHREYS

PRESSURE OIL STILL

Filed Jan. 7, 1921 3 Sheets-Sheet 3

Fig. 3.



Inventor:
Robert E. Humphreys
By Dyrenforth, Lee, Christy & Fish
Attys.

[fol. 1455] United States Patent Office

Patented May 4, 1926. 1,582,929

Robert E. Humphreys, of Whiting, Indiana, Assignor to Standard Oil Company, of Whiting, Indiana, and Chicago, Illinois, a Corporation of Indiana

Pressure Oil Still

Application Filed January 7, 1921. Serial No. 435,700

To all whom it may concern:

Be it known that I, Robert E. Humphreys, a citizen of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in Pressure Oil Stills, of which the following is a specification:

The present invention relates to oil stills, and more particularly to such stills intended for the distillation of oil under high pressure, for example, pressures of the order of 350 pounds per square inch. It will be fully understood from the following description thereof, illustrated by the accompanying drawings, in which a specific embodiment of the invention is shown.

In the drawings:

Fig. 1 is a vertical section thru the still, the setting being likewise shown in section;

Fig. 2 shows upon the left half of the figure a front elevation of the still, the front of the setting being shown in section as indicated on the line 2—2 in Fig. 1, and the right half of which shows a vertical section thru the still on the line 2^a—2^a of Fig. 1, and

Fig. 3 shows a front elevation of the still.

Referring more particularly to the drawings, the numeral 10 indicates the still setting, the parts of which will be described in greater detail in connection with the various parts of the still. In the front portion of the setting 10, a fireplace 11 or other suitable combustion chamber is provided, the combustion gases issuing therefrom being forced to travel upwardly around the arch 12 thru the main heating chamber 13 and issuing from the furnace thru the flue 14.

A plurality of drums or cylinders 15, 16, 17, and 18, which extend longitudinally of the furnace setting, are arranged thereabove and serve as containers for the bulk supply of oil undergoing distillation. These drums which may be lagged, if desired, are preferably arranged in pairs, the drums of each pair being vertically disposed one above the other, as illustrated in connection with the pairs of drums comprising 15 and 16, or that comprising drums 17 and 18. As the relative arrangement of each pair of drums is the same, that of only one pair of drums 15 and 16 will be described in detail.

The drums 15 and 16 are positioned with their axes substantially parallel to each other, and the rear ends of the drums are preferably elevated slightly above the forward ends. The drums 15 and 16 are spaced from each other, and retained in their proper relationship by the spacers or webs 19, 19 which are supported upon the lower drum 16, and upon which the upper drum 15 rests. On each side of the center line of the drums, a plurality of curved or bent pipes 20, 20 extend from the lower portion of the upper drum to the upper portion of the lower drum, these pipes or tube sections being rolled into the walls of the drums at each end. Each pair of drums is supported in swings 21, there being at least one near the front and one near the rear. These swings are suspended from the cross beams 22, which are mounted upon the uprights 23, 23. The rear wall of the furnace setting 10 is extended upwardly as indicated at 24 to a point such that it is barely cleared by the lowermost of each pair of drums and thus serves as a support for the drums in case of failure of the swings from which they are supported.

A vapor outlet 25 is provided near the rear end of each of the upper drums of the several pairs of drums, and each of these vapor outlets communicates with a vapor manifold 26. The manifold 26 is in turn provided with an outlet 27, which may communicate with a suitable vapor line or run back (not shown) connected to a condenser and the manifold 26 is likewise provided with an upwardly directed pipe connection 28 to which is attached an adjustable pressure safety valve 29.

At their forward ends each of the lower drums 16, 18 is connected by means of a downwardly depending leg 30 with a transverse, horizontal drum 31, which may suitably

be supported on the top of the furnace setting 10, as more fully hereinafter described. At their rear ends, each of the lower drums 16, 18 is provided with a depending leg or downcomer 32 by which it communicates with a lower horizontal transverse drum 33, secured in the lower portion of the furnace setting 10. A plurality of upwardly inclined tubes, 35, 35 extend from the lower drum 33 thru [fok 1456] the main combustion or heating chamber 13 to the upper drum 31. The lower drum is provided with a feed pipe 36 and a discharge pipe 37, preferably arranged near the opposite ends of the drum. Plugs, as indicated at 38, 38 may be screwed into openings in the upper transverse drum 31 and their removal permits inspection of its condition and of that of the tubes 35.

The upper transverse drum 31, in the construction illustrated, is cradled in a depression in the front portion of the roof of the furnace, preferably in a bed of granulated fire brick or similar refractory material, which is retained in position by suitable sealing plates 39. The lower transverse drum 33 is supported in a refractory brick cradle 40 between the rear wall of the furnace setting 10 and the wall 41 of the flue 14. It is protected from the heat of the combustion chamber 13 by the bed 42 of granulated fire brick or similar refractory material, which is held in position by suitable sealing plates 43.

As is readily apparent, the fireplace may be provided with suitable inspection openings 45, 45, wherever deemed desirable.

In beginning the operation of the still, the charging stock, which may be, for example, a heavy hydrocarbon oil of the character of the fuel oil distillate from mid-continent crude having a specific gravity of 32 to 34° Baumé, is charged into the still thru the feed pipe 36 until the uppermost longitudinal drums 15, 17 are partially filled. The transverse drums 31 and 33, the tubes 35, 35, the legs 30, 30, the downcomers 32, 32, the lower longitudinal drums 16, 18 and the connecting tubes 20, 20 are then completely filled with the oil. Firing is then begun and the vapors are permitted to escape freely until any water present in the charging stock has been removed. The vapor outlet 27 from the manifold 26 is then conpected with a suit-

able refluxing and condensing system (not shown), the still is placed under pressure, either antogenous or from an extraneous source, and firing continued until the stock in the still is brought to the required or desired temperature. The pressure maintained upon the still may be, for example, 250 pounds per square inch, the temperature of the stock being controlled to produce the desired rate of conversion thereof into light boiling products, for example of the gasoline type in the manner described in the prior application of Humphreys, Rogers and Paulus, Serial No. 312,398, filed July 21st, 1919. The bulk supply of the oil undergoing distillation is distributed thru the plurality of longitudinal drums, 15, 16, 17, 18, each of which is of relatively small diameter as compared with the diameter of a single drum which would be required to contain the entire bulk supply of oil. By the arrangement of the upwardly inclined tubes, 35, 35 within the combustion chamber of the furnace, and their connection with the lower transverse drum 33 and the upper transverse drum 31, each of which is connected with the longitudinal drums forming the bulk supply containers, a rapid semicyclic circulation of the stock is maintained during the entire heating period. During the distillation, fresh stock may be supplied thru the feed pipes 36, or if desired, it may be supplied thru the run back connected to the vapor outlet 27. When it is desired to conclude the distilling operation, the firing is stopped, the still and its contents permitted to cool sufficiently to permit the removal of the tar or residuum thru the discharge pipe 37, and the still may then be cleaned.

Altho the present invention has been described in connection with the specific details of an embodiment thereof, it is not intended that these details shall be regarded as limitations upon the scope of the invention, except in so far as included in the accompanying claims.

I claim:

1. In an oil still for operation under high pressure, a plurality of sets of cylindrical oil containers, each set comprising an upper and a lower container, vapor outlets from the tops of said upper containers, a transverse drum below the lower containers of the said sets and communicating with one end of each thereof, a second transverse drum below the first mentioned transverse drum and commu-

nicating with the other end of the lower containers of said sets of containers, upwardly directed tubes between said transverse drums, and means for applying heat to said tubes.

2. In an oil still for operation under high pressures, a plurality of pairs of cylindrical oil containers, the containers of each pair being arranged one vertically above the other, spacing means between the upper and lower container of each pair, a plurality of curved tubes connecting the upper and lower container of each pair and establishing free communication therebetween, a vapor outlet from the upper container of each pair, said vapor outlets being manifolded, heating means, and means for flowing a stream of oil from one of each pair of containers through the heating means and back to the pair of containers.

3. In an oil still for operation under high pressures, a plurality of pairs of parallel cylindrical oil containers, the containers of each pair being arranged one vertically above the other, spacing means between the upper and lower container of each pair, a plurality of curved tubes connecting the upper and lower container of each pair and establishing [fol. 1457] free communication therebetween, a vapor outlet from the upper container of each pair, said vapor outlets being manifolded, a cylindrical drum below the forward ends of the lower containers of the pairs of containers, a conduit from the forward ends of each of said lower containers to the drum, a second cylindrical drum below the rear ends of the said lower containers and at a lower level than the first mentioned drum, a conduit from the rear end of each of said lower containers to the second drum, a plurality of upwardly inclined tubes between the drums, and means for heating the tubes.

4. In an oil still, a pair of cylindrical oil containers arranged one vertically above the other, spacing means between the containers, tubes between the containers and establishing free communication therebetween, elevated supports, and depending swings suspended from said supports in which the containers are supported.

5. In an oil still, a pair of cylindrical oil containers arranged one vertically above the other, spacing means between the containers, tubes between the containers and

establishing free communication therebetween, elevated supports, depending swings suspended from said supports in which the containers are supported, a furnace setting below the containers, a wall of the setting being extended upwardly to slightly below the lowermost of the containers, heating means within the setting and means for conducting a stream of oil from the containers through the setting and back to the containers.

6. In an oil still for operating under high pressures, a heating chamber, upper and lower transverse cylindrical drums exterior of said chamber, means placing the interiors of said drums in communication and extending through the heating chamber, pairs of longitudinal containers above and exterior of said heating chamber, a conduit connecting one end of one of each of said pairs with the upper transverse drum and conduits connecting the other end of one of each of said pairs with the lower transverse drum, said last named conduits being exterior of said chamber.

7. An oil still for operation under high pressure comprising, in combination, a heating chamber, transverse oil drums above and below said chamber, means passing through the chamber, affording free communication between said drums, a plurality of sets of inclined vertically spaced cylindrical containers above said upper transverse drum, means establishing free communication between the containers of said sets, other means providing free communication between the lower end of the lowermost container of each set and the uppermost transverse drum, and other means exterior of said chamber establishing free communication between the upper end of the lowermost container of each of said sets, and the lowermost transverse drum.

8. In a still for cracking oil, a heating chamber having a furnace connected thereto, an upper and lower drum located outside said heating chamber and furnace, tubes connecting the drums and passing through the heating chamber, storage drums above and outside said heating chamber, and connections between said storage drums and said upper and lower drum, located outside said chamber.

9. In a still for cracking oil, a heating chamber having a furnace connected thereto, an upper and lower drum located outside said heating chamber and furnace, tubes connecting the drums and passing through the heating chamber, storage drums above and outside said heating chamber, and connections between said storage drums and said upper and lower drum, located outside said heating chamber, the combustion chamber of said furnace being constructed and arranged so that the tubes are protected from the direct radiant heat of the furnace.

10. In a still for cracking oil, a heating chamber having a furnace connected thereto, an upper and a lower transverse drum located outside said heating chamber and furnace and extending beyond both said walls thereof, tubes extending through said heating chamber and connecting the upper and lower drums, longitudinal drums located above said furnace, and connections between said longitudinal drums and said upper and lower drums, said connections being located entirely outside said heating chamber and said furnace.

11. In a still for cracking oil, a heating chamber having a furnace connected thereto, an upper and a lower transverse drum located outside said heating chamber and furnace and extending beyond both side walls thereof, tubes extending through said heating chamber and connecting the upper and lower drums, a pair of longitudinal drums each located above an end of said upper drum and connections between each end of said upper drum and one of said longitudinal drums and between each end of said lower drum and one of said longitudinal drums.

12. In a still for cracking oil, a heating chamber having a furnace connected thereto, an upper and a lower transverse drum located outside said heating chamber and extending beyond both side walls thereof, tubes extending through said heating chamber and connecting the upper and lower drums, a pair of longitudinal drums each located above an end of said upper drum and connections between each end of said upper drum and one of said longitudinal drums and between each end of said lower drum and one of said longitudinal drums, said connections and [fol. 1458] said tubes being constructed and arranged so

that the resistance to flow in said connections is not greater than the resistance to flow in said tubes.

13. In a still for cracking oil, a pair of horizontally extending storage drums arranged one above the other and connected by a series of nipples spaced along their length and arranged to permit a free circulation of the oil between the drums, the lower drum having an oil inlet at one end and an oil outlet at the opposite end constructed and arranged to produce a general circulation of oil through the drum and longitudinally thereof.

14. In a still for cracking oil, a pair of horizontally extending storage drums arranged one above the other and connected by a series of nipples spaced along their length and arranged to permit a free circulation of the oil between the drums, the lower drum having an oil inlet at one end and an oil outlet at the opposite end constructed and arranged to produce a general circulation of oil through the drum and longitudinally thereof, said nipples being curved to permit expansion without undue strain on the connections between the nipples and the drums.

15. In a still for cracking oil, a pair of horizontally extending storage drums arranged one above the other and connected by a series of nipples spaced along their length and arranged to permit a free circulation of the oil between the drums, the lower drum having an oil inlet at one end and an oil outlet at the opposite end constructed and arranged to produce a general circulation of oil through the drum and longitudinally thereof, at least the upper storage drum being inclined to provide a vapor and gas outlet near the highest end of the drum and the oil inlet and outlet of the lower drum being arranged to cause the general circulation of oil through the drums in a direction toward said vapor and gas outlet.

16. In a still an upper and a lower transverse drum, heating tubes connecting the transverse drums, a longitudinal storage drum above the ouper transverse drums, connections between the upper and the lower transverse drums and the longitudinal storage drum, and a furnace to heat the tubes, constructed and arranged so that all of the drums and their connections other than the heating tubes

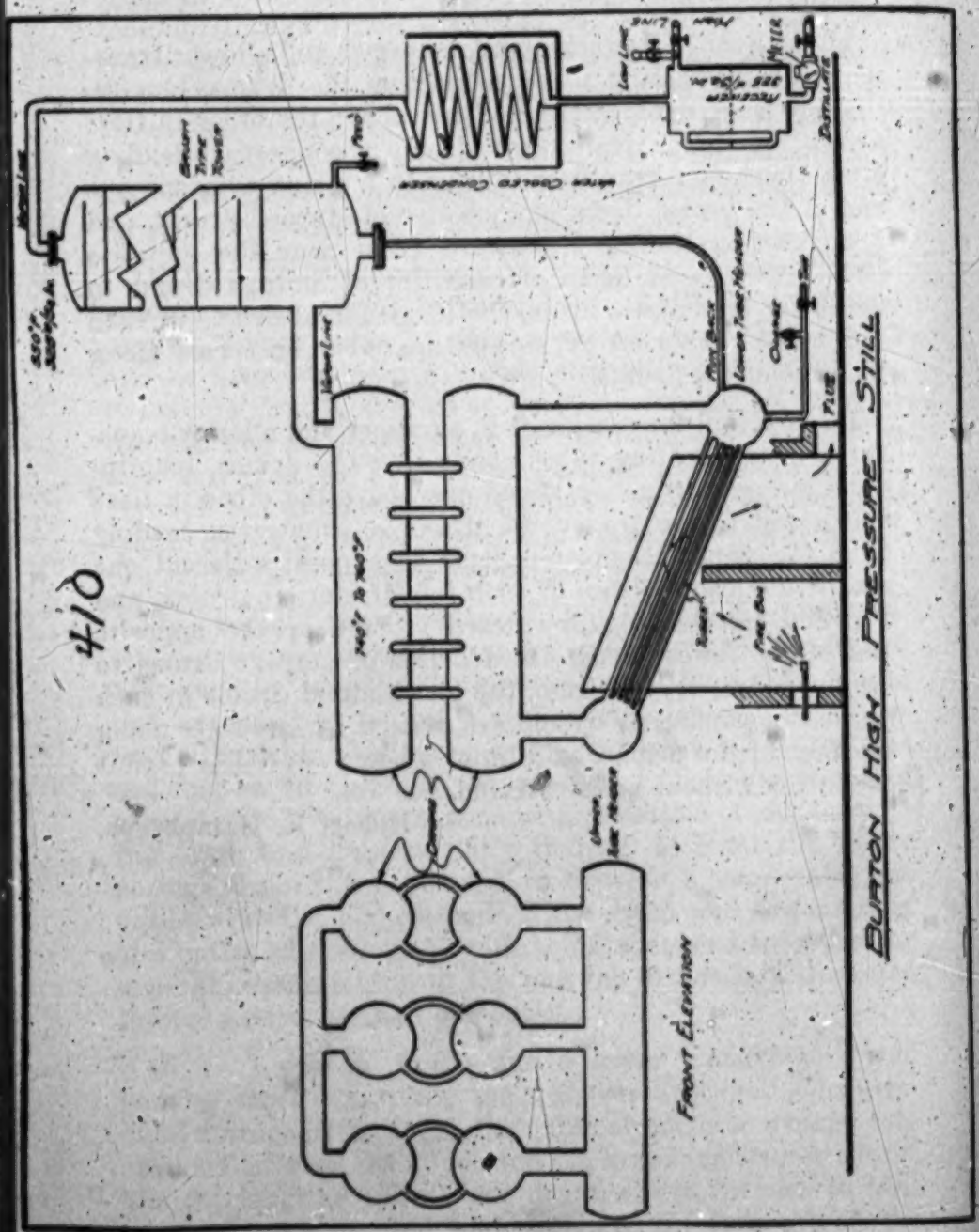
are protected from the heat of the furnace, said longitudinal storage drum being inclined to form a vapor space at one end thereof and a vapor outlet in said drum connecting with said space.

17. In a still for cracking oil, an upper and a lower transverse drum, heating tubes connecting the drums, longitudinal storage drums arranged one above the other in tiers above the upper transverse drum, a connection leading from the upper transverse drum to a point adjacent one end of the lowest drum of each tier of storage drums, and a connection leading downward from near the opposite end of the lowest drum of each tier of storage drums to the lower transverse drum, the longitudinal drums in each tier being connected by nipples spaced at intervals along the axes of the drums.

18. In a still for cracking oil, an upper and a lower transverse drum, heating tubes connecting the drums, longitudinal storage drums arranged one above the other in tiers above the upper transverse drum, a connection leading from the upper transverse drum to a point adjacent one end of the lowest drum of each tier of storage drums, and a connection leading downward from near the opposite end of the lowest drum of each tier of storage drums to the lower transverse drum, the longitudinal drums in each tier being connected by nipples spaced at intervals along the axes of the drums, said nipples being curved to permit expansion without undue strains.

Robert E. Humphreys.

[fol. 1459] EXHIBIT No. 440



[fol. 1460] Exhibit No. 411 appears on page 501 of the Master's report.

[fol. 1461] Exhibit No. 412 appears on page 499 of the Master's report.

[fol. 1462] Exhibit No. 413 appears on page 490 of the Master's report.

[fol. 1463] EXHIBIT No. 414

United States Patent Office

James S. Lang, of Boston, Massachusetts

Process for Removing Snow

No. 863,855. Specification of Letters Patent. Patented Aug. 20, 1907

Application Filed June 2, 1906. Serial No. 319,948

To all whom it may concern:

Be it known that I, James S. Lang, of Boston, in the county of Suffolk and State of Massachusetts, a citizen of the United States, have invented a new and useful Process for Removing Snow, of which the following is a full, clear, and exact description.

The especial object of my invention is the employment of a process by which snow in a soft or loose condition may be removed under circumstances where it could ordinarily be removed only by the expenditure of much time and labor, as for example,—from railroad switches which in order to work properly must be kept clear of snow; or from manholes, hydrants or other places where despatch in removing snow may be of the — importance.

The process consists in sprinkling upon the snow over the object on or in which the snow or ice has accumulated an inflammable fluid having such volatility that when distributed

on soft or loose snow it will volatilize or evaporate with sufficient rapidity to maintain a continuous flame when the vapor from the fluid is ignited; then igniting said vapor, the heat thereof melting the snow.

I have found that in order to remove soft and loose snow by the above process the fluid used must have such volatility that it will volatilize with sufficient freedom to maintain a continuous flame at a temperature of 32° F. or under, because when the fluid is distributed upon soft or loose snow it sinks into the snow and if, like gasolene, it does not volatilize with sufficient freedom under these conditions to maintain a continuous flame, the fluid is absolutely useless for removing snow.

I have found that liquefied gas, a fluid hydrocarbon product obtained from the high compression of Pintsch gas and having a degree of volatility much higher than gasolene, will freely volatilize at a temperature of 32° F. or under, and is not only a cheap but an especially good material for effecting the purpose of my invention inasmuch as it rapidly volatilizes under the conditions above referred to.

In practice the process is an especially effective one. The volatile liquid after it is sprinkled upon the snow will percolate through it, the snow acting as a sponge for retaining the fluid, which rapidly volatilizes. The vapor when ignited will burn for a long time or until the fluid has entirely volatilized during which time the heat from the flame not only melts the snow but dries the object upon or in which the snow has accumulated.

Having thus fully described my invention, I claim and desire to secure by Letters Patent of the United States:

1. The process of removing soft or loose snow consisting in applying to snow of the above character an inflammable fluid having such volatility that when distributed upon soft or loose snow it will volatilize with sufficient freedom to maintain a continuous flame when the vapor from the fluid is ignited, and igniting such vapor.

2. The process of removing soft or loose snow consisting in applying to snow of the above character an inflammable fluid of such volatility that at a temperature of 32° F. or under it will volatilize with sufficient rapidity to maintain

a continuous flame when the vapor from the fluid is ignited, and igniting such vapor.

3. The process of removing soft or loose snow consisting in applying to snow of the above character a highly volatile inflammable fluid product obtained from the compression of Pintsch gas, and igniting the vapor of such fluid product.

James S. Lang.

Witnesses: John E. R. Hayes, M. E. Flaherty.

[fol. 1464] EXHIBIT No. 415

Oct. 15, 1926. Walter N. Carpenter, Shorthand Reporter

Description Filed in Support of an Application for Patent

Presented by George Danré, Civil Engineer, Marseille, Pieree Fortuné Victor Mouillard, Proprietor, 15 rue des Petites Ecuries, Paris, and Pierre Adrien Mercier, Proprietor, 15 rue Bac, Paris

Filed December 23, 1856. Delivered on February 18, 1857

No. 30263

For "The Compression of Lighting Gas by Pressure at the Time of Production"

The important novelty embodies in the operations which we shall describe and for which we now claim a patent is:

1st. The combination of all of the work which we perform to obtain the compression of the lighting gases by the natural compression of the gases obtained from the liquid or solid materials simultaneously with their production.

2nd. The use of a preliminary decomposition of the oil into oil vapor or of a suitable way to obtain the simultaneous production of the gases over a large contact surface, so as to avoid the fouling which is ordinarily caused when this transformation takes place by contact at one point only.

3rd. The heating of the retorts especially by means of gases, this heating being regulated by dampers in ordinary

heating arrangement and by valves in gas heating arrangement, so as to obtain without variation temperatures that are always the same.

4th. By throwing back the oil vapors against the walls of the transformation retorts with the aid of plates of iron, metal clay or some other suitable material, or with the aid of any other kind of device that will throw them back.

5th. The maintenance of a higher pressure, such as, for instance, 25 atmospheres, through the natural and simul- [fol. 1465] taneous production of the gas obtained by the transformation of the oils into vapors and the communication of the feeding and producing vessels.

Having thus set forth the most salient points of our invention, we will state in detail the operation of our system with the aid of the attached drawings which are hereinafter explained.

Explanation

Fig. 1 is a general section of the apparatus as a whole.

Fig. 2 is a front elevation, partly in transverse section.

Fig. 3 is a plan.

A.—Cylinder, made of copper or brazed sheet-iron, oil reservoir.

B.—Small tube intended for the introduction of the oil into the cylinder A. through a funnel momentarily replacing the screw plug b.

C.—Pipe, serving to establish on the oil of the cylinder A. a pressure equal to that which is formed below.

D.—Regulating valve for letting the oil run into the vertical retort F.

E. Glass tube or lantern, showing the stream of oil which it is desired to let run into the vertical retort F.

F. Wrought-iron retort, filled with scrap iron or waste pieces of sheet-iron, arranged in such a way as to leave much free space.

H H′ H″ three tube sections; H, communicating with the lantern E, H′ with the inclined retort I, and H″ with the inclined retort J.

I J.—Wrought-iron retorts, of sufficient thickness to withstand a pressure of 30 atmospheres, even under the

influence of the expansion of the bright cherry red heat, to which nevertheless they should not be submitted, that of the ordinary cherry red being the maximum heat which is to be employed.

K K′ K″ Cast iron stars, placed in the retorts in such a way that the rays are staggered, in order that the oil vapors may be directed against the walls and present to them the greatest possible decomposing surfaces.

L L′—Pipes connecting with cylinder M.

M.—Copper or sheet-iron cylinder serving as condenser and as holder for the condensate.

N.—Cooling pipes, carrying the gas to a second condenser O.

[fol. 1466] O.—Cylinder similar to M. having the same purpose and furnishing the compressed gas to the cylinder A. through the pipe C.

P.—Pipe conducting the compressed gas to the pressure gauge Q.

Q.—Pressure gauge indicating the pressure of the gas.

R.—Pipe carrying the compressed gas to the omnibus or truck S.

S.—Omnibus or truck, containing from 1 to 10 cylinders made of sheet-iron or copper.

T.—Pipe carrying the gas to a temporary storage cylinder, placed under ground or on the ground and serving to lower the pressure which exists in the apparatus while the omnibus or tender, the reservoirs of which are full of gas, is removed, and while another whose cylinders are empty is brought around.

U.—Pipe carrying to a gasometer the gas which remains in the apparatus after having established the equality of pressure with the omnibus or tender, the cylinders of which were empty. This operation takes place only when the gas flowing back in the lantern E and preventing the oil from flowing shows that a general cleaning has become necessary.

V.—Valve serving to put the gasometer into communication with the apparatus.

X.—Valve serving to retain the gas in the apparatus when the omnibus is changed and when the gas is sent into the temporary storage cylinder through the pipe T, or when the entire apparatus is being emptied by sending the

gas to the gasometer through the pipe U, the valve V being open after the pressures have first been balanced in the cylinders of the omnibus or tender which are to be charged.

From 4 to 10, pipes welded to the extreme end of the pipe R. by means of a T-pipe or of any other connection.

Z Z'.—Valves serving to empty the condensates deposited in the cylinders M and O.

Preliminary Applications

The apparatus just described in the foregoing is to be preferably entirely of wrought-iron in the part subjected to the immediate action of or near the fire, and the joints, to be well made, must be of soft copper rings pressed between two well-connected flanges.

The parts which, being subjected to the action of the fire [fol. 1467] in a less immediate manner, will become heated only through the contact of the oil vapors not converted into gas; may be of copper or brazed sheet-iron, and the joints may be appropriately made by means of zinc or lead gaskets, according to the degree of heat they have to resist.

These joints present this advantage that, as the heat rises in accordance with the pressure, the gaskets will melt, will allow the gas to escape and will thus serve as safety valves, if in the apparatus that is intended to be operated at a maximum of 25 atmospheres through inattention of the operator the pressure should rise to 30 atmospheres.

Hence no explosions need be feared: there will always be a weak part which will give way and permit more gases to escape under a stronger pressure than can be produced by the oil which flows through lantern E.

On the other hand, this stream of oil can cause only a limited and gradual production and compression of gas limited and gradual, and never an immense and sudden production; hence there is on possibility of an explosion.

Beyond the valve X, the tubes which establish the communication with the tender or omnibus may be of lead, the advantageous flexibility of the metal in this part of the apparatus not excluding the resistance to an internal pressure of 20 to 30 atmospheres.

Pressure

The pressure of twenty-five atmospheres under which the hot gas enters the portable cylinders, which pressure is reduced by cooling to twenty atmospheres when the omnibus or tender is separated from the apparatus, is the usual pressure under which the apparatus should be operated.

In fact, this apparatus and its connections are calculated to resist thirty atmospheres at the maximum and then, because the compression of the gas takes place gradually and without shock, the gas does not decarburate under this pressure of twenty-five atmospheres when it is hot, and under that of thirty atmospheres when it is cold.

This inconvenience begins to manifest itself entirely above advantageous flexibility of the metal in this part of the apparatus and of the operation imposes the limits by which we are stopped.

[fol. 1468] Decomposition of the Oils

When, following the old method, the stream of oil is introduced into the generator of gas; this oil, arriving always on the same spot, whatever means may be employed, promptly creates there a deposit forming a sponge which absorbs more and more of the new oil which enters and hinders its decomposition.

Becoming thicker, little by little, this sponge obstructs the generator after a few hours. This inconvenience is all the more serious in the present operation because the generators, to preserve a sufficient resisting strength under the double influence of the high pressure of twenty-five atmospheres and of the dark cherry red heat, can have only a small diameter.

It would, therefore, be necessary to clean often, which causes more work than in the manufacture of oil gas at ordinary pressure.

To obviate this inconvenience, we have recourse to a preliminary formation of the oil into oil vapors in the vertical retort F and it is no longer the oil but the oil vapors which, entering one, two or several inclined retorts, are developed there, and on coming into contact with all the heated walls, become converted into gas more quickly and more efficaciously than by the old system.

Hence, it will require a much longer time to clog the generators so that two cleanings every twenty-four hours instead of four or five will be sufficient.

One is warned of the necessity for cleaning when, the pressure being greater in E than in C, the oil stops running and one sees clearly the gas which was not seen in the glass tube while the pressure equilibrium existed.

Heating

The heating of three retorts may take place by ordinary means, but heating by heating gas is preferable on account of the variations of heat to which the operator must give close attention. Thus, the heat increasing in the entire apparatus in proportion as the pressure of the gas rises, it is proper to decrease the fire little by little so that, the heat of the vertical retort F, which is cherry red in the beginning under the pressure of O to 1 atmosphere, a gradual decrease will bring it to reddish brown for F and dark cherry red for I J when the pressure gauge indicates twenty-five atmospheres.

[fol. 1469] This operation, which can only be carried on with the aid of a combination of dampers for ordinary heating and with much waste heat, becomes at once easy and economical by heating with gas, since the operator lowers the flames of the gas, at will, by a valve, by touching his valve only as often as is needed to make use of the stoker in the ordinary heating, he will, without becoming tired and with a little willingness, carry out his duties.

Description

Cylinder A being full of oil, plug *b* screwed on, the plugs of the retorts in place and all the connections of the apparatus secure, valve V being closed and also that of the storage cylinder at the extreme end of pipe U, valve X being open and also those of the portable cylinders, the retorts being at the degree of heat previously indicated, a stream of oil, that will furnish about thirty liters an hour, is caused by the regulating valve D to flow through the glass tube E.

This stream of oil will produce about twenty cubic meters of gas an hour, a quantity consistent with the proportions of the apparatus.

The oil enters the vertical retort F, the temperature of which is sufficient to vaporize this oil which spreads over all the heated surfaces without having time to become transformed in a single place into a thick obstructing mass.

The oil vapors are forced by the increasing pressure into the generators, I J, in which stars of cast iron, or fire-clay, are arranged in such a way that their rays are staggered (opposed) which arrangement directs the vapors continuously against the inner walls of the retort. This device in combination with the fact that the heat increases with the pressure, makes it unnecessary to bring the retort up to a high temperature in order to heat its center: it is enough that the interior walls of the retort be sufficiently heated to decompose the oil vapors and intimately combine the gases which, if separated, would be carbureted at different degrees.

From the retorts I and J the gas enters the cylinder M, begins to cool and deposits there a part of its condensate: from M it passes into O, where it cools still more and deposits more condensate.

Cylinders M and O could be made as true condensers cooled by atmospheric air and water, by placing pits below and sieves above into which cold water would enter continuously which would then fall as rain on the said cylinders. [fol. 1470] From the cylinder O the gas is forced by pressure into the portable cylinders placed on a wagon, an omnibus or tender. At the same time the compressed gas is carried, by its pressure through the pipe C into the oil reservoir A where it presses on the oil with a force equal to that which accumulates continuously in all the rest of the apparatus, so that the stream of oil would continue to flow with the same volume whatever the pressure within the apparatus.

By giving the vertical retort F a little more height, it is possible to introduce into it a hundred kilograms of tar, rosin, pitch, boghead (gas coal) or every other oily body which is not sufficiently fluid.

The vapors obtained, which compress themselves of their own accord, will pass into the inclined retorts I and J and will follow the same phases of conversion into compressed gas, and will cause it to pass into all the empty and communicating portions of the apparatus; their condensates,

settled and suitably purified, will be poured into the reservoir A.

After having evaporated the hundred kilograms of materials placed in the vertical retort F, the reservoir A having first been filled either with oils as in the first operation described, or with condensates coming from different preceding distillations of thick materials, the operation may then be continued through equalizing of pressures by opening the regulating valve D and letting the liquid run in the manner hereinbefore described.

What constitutes in the operations heretofore described as incontestable invention is a combination that is obviously the logical result of practical and repeated, long-continued and costly study.

A simple modification in the mechanical forms could not invalidate this invention which it could be possible to bring to this degree of simplicity and practical facility without any danger at the cost of much time, money and effort of every kind to its inventors.

Paris, December 23, 1856,

Danre Moullard & Mercier, by Ricordeau, Attorney.

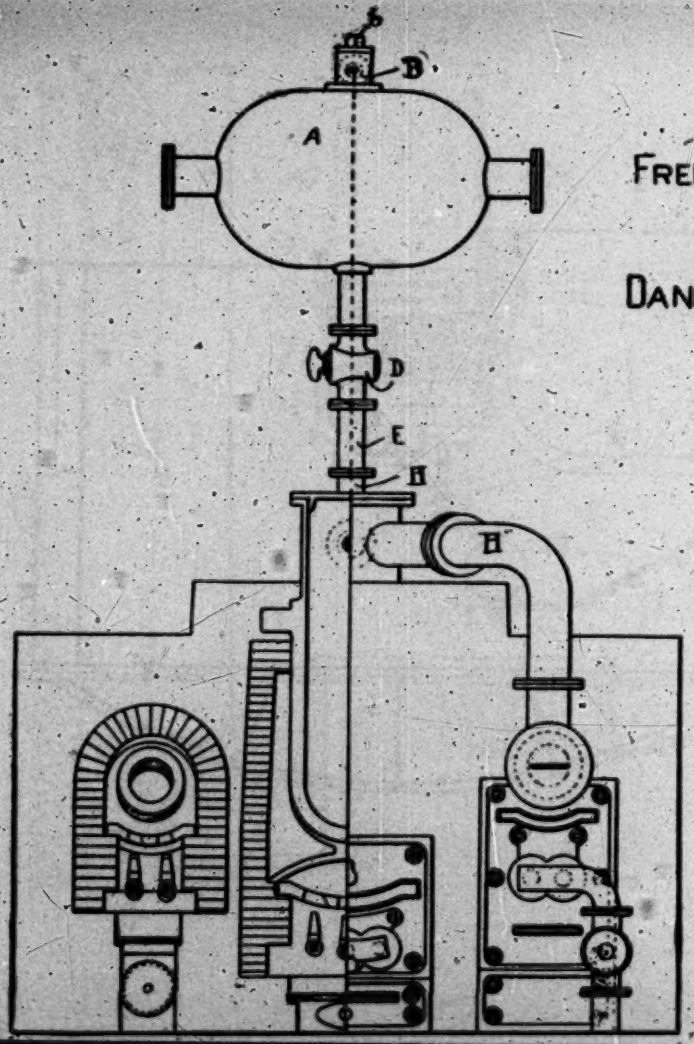
FRENCH PATENT - 30,263

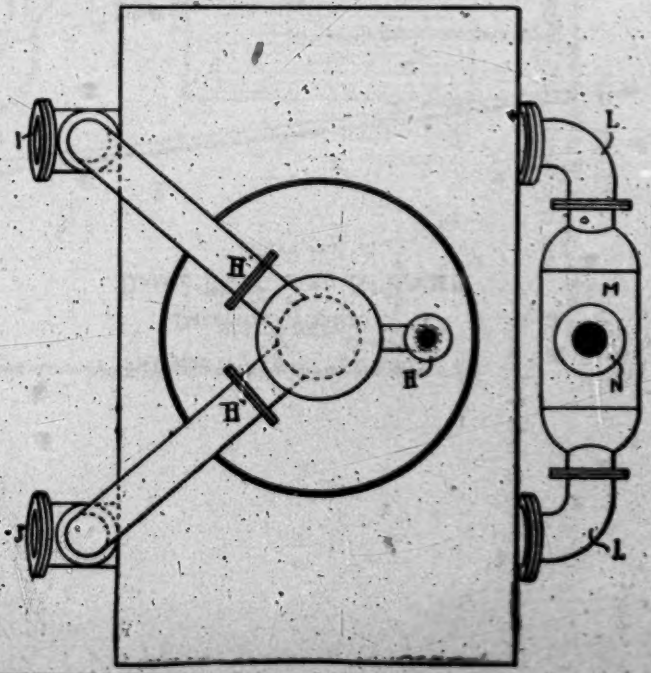
of

December 23, 1856.

DANRÉ MOUILLARD & MERCIER.

(SHEET Nº 2)





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[fol. 1472]

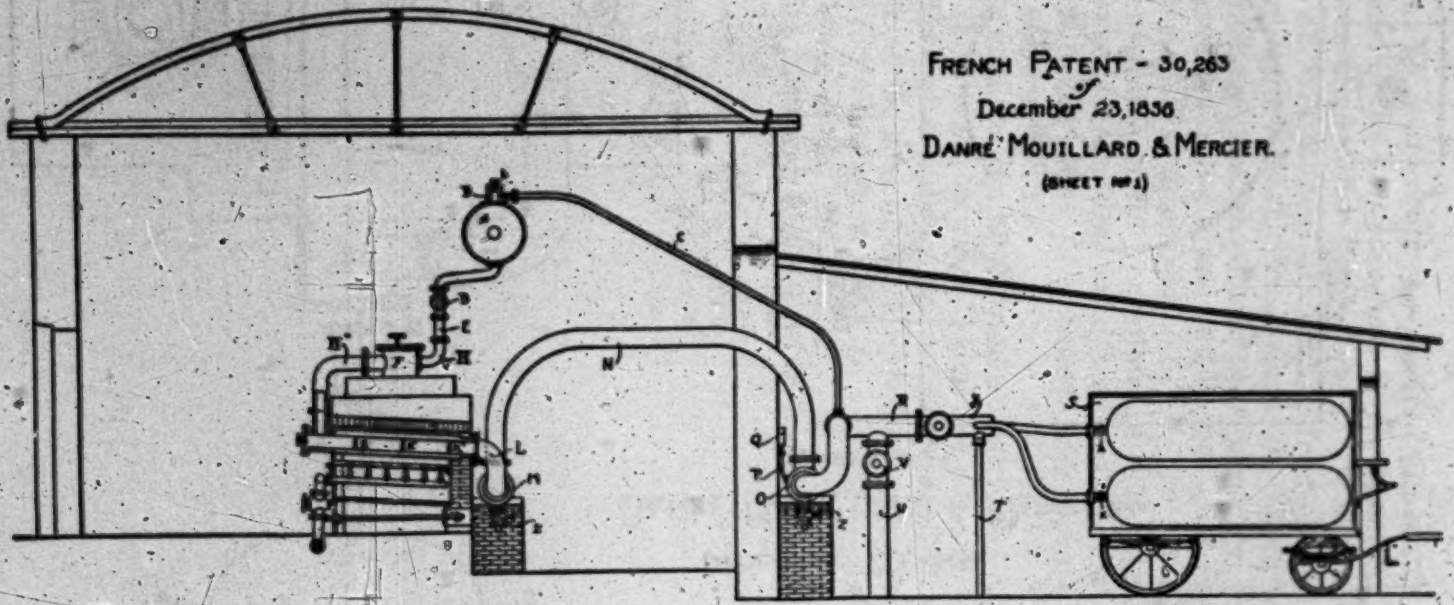
FRENCH PATENT - 30,263

of

December 23, 1856

DANRÉ MOUILLARD & MERCIER.

(SHEET NO 1)



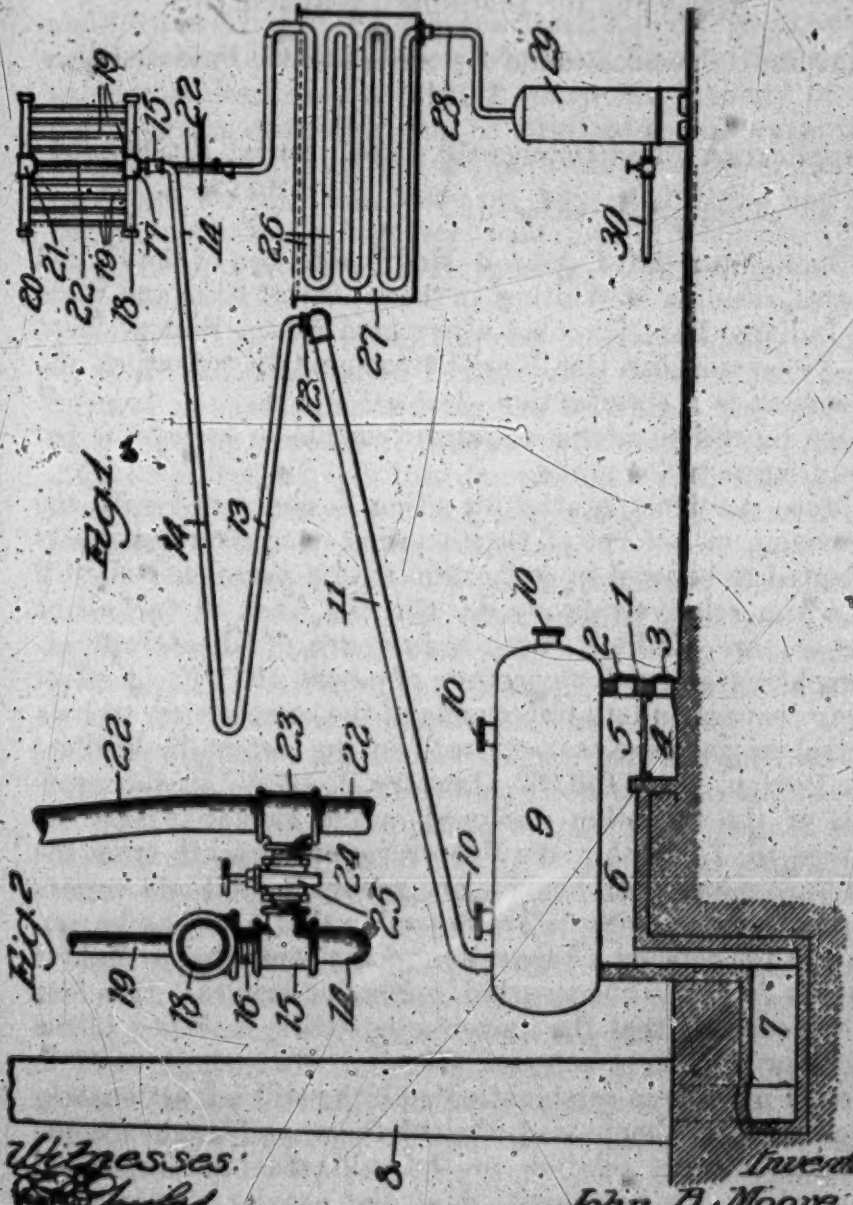
[fol. 1473] EXHIBIT No. 416

J. B. MOORE.

APPARATUS FOR DISTILLING PETROLEUM OILS.

APPLICATION FILED OCT. 19, 1914

1,130,318. Patented Mar. 2, 1915



[fol. 1474] United States Patent Office

John B. Moore, of Whiting, Indiana, Assignor to Standard Oil Company, of Chicago, Illinois, a Corporation of Indiana

Apparatus for Distilling Petroleum-Oils

1,130,318. Specification of Letters Patent. Patented Mar. 2, 1915

Application Filed October 19, 1914. Serial No. 867,456

To all whom it may concern:

Be it known that I, John B. Moore, a citizen of the United States, residing at Whiting, in the county of Lake and State of Indiana, have invented a new and useful Improvement in Apparatus for Distilling Petroleum-Oils, of which the following is a specification.

My invention relates to improvements in apparatus for distilling petroleum oils.

More particularly, the invention is concerned with the provision of a form of fractionating condenser especially adapted to be used in connection with a petroleum oil still in which relatively heavy paraffin oils, such as fuel-oil or gas-oil, are distilled under a pressure of about four atmospheres and a temperature of about 700° F. to effect their conversion into lighter oils of the same series, such as petrol or gasolene, as set forth in the patent to William M. Burton, No. 1,049,667, January 7, 1913. In the practice of the invention disclosed in the Burton patent referred to, I find that the lighter vapors passing from the still are mixed with heavier or unconverted oil and vapors thereof, and it is therefore desirable that a means be employed for causing a separation of the converted or lighter vapors from the unconverted or heavier vapors. It is further desirable that the unconverted oil be returned to the still for further treatment therein. With these ends in view, I provide in combination with the still a fractionating condenser of simple and efficient form, and so mount the condenser with relation to the still that the liquid oil formed by the condensation of the heavier vapors may drain or run back continuously and as it is formed to the still, there to undergo further treatment.

It is to be particularly noted in connection with my invention that the apparatus is so constructed and arranged that the condensation of the heavier vapors and the return of the liquid formed thereby to the still, goes on simultaneously and continuously, a single set of passages serving for the outward flow and fractional condensation of the vapors, and the inward flow of the unconverted liquid formed by the condensation of the heavier vapors. It will further be noted that I provide means by which the capacity of the fractionating condenser may be adjusted to suit variations in running conditions and temperature changes of the atmosphere, so that the condenser may at all times and under all conditions act to fractionate out or condense all of the heavier vapors without causing condensation of the lighter vapors.

In order that my invention may be more readily understood, I will describe in considerable detail a particular form of apparatus embodying the invention, and which I have found in practice to operate satisfactorily to produce the results desired. In this description I shall refer to the accompanying drawing which illustrates a preferred embodiment of the invention described.

In the drawing Figure 1 is a diagrammatic view in elevation of a petroleum still, fractionating condenser, main condenser and distillate receiving-drum. Fig. 2 is an enlarged side elevation of the by-pass by which the capacity of the fractionating condenser may be adjusted.

Referring more particularly to the drawing, the numeral 1 designates a furnace of ordinary construction and having the usual fire-door 2, ash-pit door 3, ash-pit 4, grate 5, combustion chamber 6, outlet flue 17 and stack or chimney 8. Mounted over and forming the upper wall of the combustion chamber 6 is the horizontal cylindrical still 9, also of standard construction and provided with the usual manholes 10 by which access may be had to the interior of the still for cleaning, filling and inspecting the same.

Leading from the upper side of the still near the rear end thereof is the upwardly-inclined vapor-outlet-pipe 11. As shown in the drawings, this pipe at its upper end is reduced in section as by the reducing connection 12 and communicates with a second upwardly-inclined pipe 13, which, for the sake of compactness of arrangement, inclines backwardly to lie over the pipe section 11. The section 13 is

in turn surmounted by a third upwardly inclining section 14, and at the upper end of the latter section I provide a T-coupling 15. The upper end of the T-coupling 15 is connected, as by a nipple 16, to a second T 17 which carries the horizontally arranged header 18. Extending upward from this header are a number of relatively small pipes 19 which [fol. 1475] are in turn connected at their upper ends to an upper header 20. The middle portion of the header 20 is connected with a T-coupling 21 in the vertical leg of which is mounted the outlet-pipe 22. As best shown in Fig. 2, this pipe extends down at a slight angle to the plane of the harp-shaped radiator or condenser formed by the pipes 19, and at a point opposite the T-coupling 15 it is provided with a T 23 facing the T 15 and connected therewith by a short pipe section 24 carrying a valve 25. It will be noted that the pipe section 24 forms a by-pass around the radiator. Below the coupling 23 the outlet-pipe 22 extends downwardly and is connected to a main condenser 26, preferably mounted in a water bath 27. The condenser 26 drains at its lower end into a connection 28 leading to the receiving drum 29. A valve draw-off pipe 30 is tapped into the lower end of the receiving-drum 29 and carries the distillate to storage tanks or reservoirs.

The operation of the apparatus described above is as follows: The still 9 containing the heavy hydrocarbon oil which is to be treated, is maintained at a temperature of approximately 700° F. at a pressure of about four atmospheres, as set forth in the Burton patent above referred to, and under such operating conditions, the heavy oil within the still undergo chemical changes by which lighter oils are formed, the vapors of the lighter oils pass out to the outlet-pipe 11, and, as before stated, I find that these vapors are intermixed with a certain percentage of unconverted vapors. The mixed volume of vapors passes upwardly and in succession through the pipes 11, 13 and 14 into the radiator formed by the upper and lower headers 18 and 20 and the connecting verticals 19. During the whole of this course the vapors are subjected to the cooling action of the walls of the various pipes, which pipes being exposed directly to the atmosphere, and without heat insulation of any kind, are maintained at a temperature considerably lower than the distillation temperature. The pipes 11, 13 and 14 and the radiator 19 therefore serve as

an air condenser, and the capacity and temperature of this condenser, formed as described, is such that by the time the vapors reach the upper header 20 of the radiator all of the heavier vapors have become condensed by contact with the relatively cool walls of the pipes. It will be understood that the heavier oils in general have boiling points higher than the lighter oils and it is therefore possible for this fractionating method to effectively separate out and condense the heavier vapors without condensing any substantial proportion of the lighter vapors. As the heavier vapors are condensed on the walls of the pipes they flow downwardly by gravity and return to the still 9, in which they are again subjected to the converting action of the still. There is thus a continuous upward flow of mixed vapors through my fractionating condenser, and a continuous downward flow of the condensed heavier fractions, these flows taking place simultaneously in the same set of passages. The lighter or converted vapors, which reach the upper header 20 of the radiator without being condensed, then pass downwardly through the pipe 22 into the condenser 26. It will be understood that this condenser is maintained at such a temperature by its water bath 27 as to effectively condense the lighter vapors. When so condensed this lighter distillate drains downwardly through the pipe 28 into the receiving drum 29, from which it is led to storage reservoirs by the draw-off pipe 30.

The rate at which distillation, i.e., evolution of vapors within the still 9, goes on, varies to some extent with the length of the run; that is, at the beginning of a run with a fresh charge filling the still the distillation will proceed more rapidly than at the end of the run when practically all of the oils have been converted. The quantity of vapors passing through the outlet-pipes which form my fractionating condenser therefore varies to an appreciable extent during the continuance of the run, and since the capacity of the fractionating condenser should be in proportion to the rate of distillation, I find it preferable to provide a means by which the capacity of the condenser may be adjusted. Changing atmospheric temperatures afford another variable factor effecting the capacity of the condenser. With these two variable conditions in mind, I provide the by-pass pipe 24 connected directly across between the vapor-outlet-pipe section 14 and the section 22 leading

to the water-condenser 26. Thus, when the distillation is proceeding at its maximum rate the valve 25 may be kept closed and the whole of the vapors evolved must therefore traverse the full length of the system. As the rate of distillation grows less, or lower atmospheric temperatures render such a large capacity for the fractionating condenser unnecessary, I may open the valve 25 and thus short-circuit or by-pass the radiator. The vapors will then pass in a large part directly across through the by-pass from the upper end of the inclined pipe section 14 to the water-condenser-pipe 22. A certain proportion of the vapors will, of course, continue to traverse the radiator, and if this is regarded for any reason as seriously effecting the efficiency of the apparatus, I may provide positive cut-off valves which will cast out the radiator and prevent access of vapors thereto.

[fol. 1476] By the operation of the apparatus described above, I find it possible to effectively prevent an appreciable proportion of unconverted heavier oils reaching the water-condenser 26. The quantity of the distillate draining into the receiving-drum 29 is therefore greatly improved. The continuous nature of the process carried on by means of this apparatus is also a decided advantage. This continuous operation is rendered possible by reason of the fact that the vapor-outlet-pipes forming the fractionating condenser of the still are all inclined upwardly so that as condensation takes place the condensed liquid continuously drains back to the still. I am thereby enabled to drain the condensed liquid back by gravity and to dispense with any pressure-pump.

While I have shown and described a particular form of apparatus embodying my invention, it is to be understood that such showing and description is illustrative only, and that I do not regard my invention as limited to these specific details except in so far as I have included such limitations within the terms of the following claim, in which it is my intention to claim all novelty inherent in the invention as broadly as the prior art will permit.

What I claim as new and desire to secure by Letters Patent is:

The combination, with a petroleum oil still, of an air condenser in the form of a vapor outlet pipe inclining up-

wardly therefrom, a header above and connected with the upper-end of said pipe, upwardly extending condenser tubes in communication with said header at their lower ends whereby the liquid condensed in said condenser tubes drains backwardly through said inclined pipe, a second header connecting the upper ends of said condenser tubes, a vapor outlet pipe extending downwardly from said upper header, a by-pass pipe connecting said first-named and second-named vapor pipes below the said first named header, means for controlling the flow of vapors through said by-pass pipe, and a second condenser in communication with said last-named vapor pipe, for the purpose set forth.

John B. Moore.

In presence of W. E. Warwick, Wm. Burton.

[fol. 1477] Exhibit No. 417 appears on page 605 of the Master's Report.

[fol. 1478] EXHIBIT No. 418

Oct. 19, 1926. Walter N. Carpenter, Shorthand Reporter

Technical Paper 181. Petroleum Technology 42

Department of the Interior

Franklin K. Lane, Secretary; Bureau of Mines, Van H. Manning, Director

B. F. Carver

Determination of Unsaturated Hydrocarbons in Gasoline By E. W. Dean and H. H. Hill

(Cut)

Washington: Government Printing Office. 1917

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First edition. November, 1917.

[fol. 1480] Determination of Unsaturated Hydrocarbons in Gasoline

By E. W. Dean and H. H. Hill

Introduction

At present one of the most important factors in gasoline production is the so-called pressure cracking process. As the transformation of heavy petroleum products into motor fuel is one of the most desirable methods of increasing the country's supply of gasoline and preventing the threatened shortage of this necessary fuel, much attention has been given to that branch of petroleum technology, with the result that many cracking processes, employing various procedures, have been devised.

Of the various cracking processes known in September, 1917, only one had attained any considerable commercial development. This single process, however, which is owned and controlled by an oil company, is so extensively operated that it is estimated to have produced 3,000,000 barrels of gasoline out of the total 41,000,000 marketed during the calendar year 1915.[a]

Cracked petroleum products, as first made, contained noticeable percentages of olefins or unsaturated hydrocarbons. Such constituents were formerly considered undesirable in gasoline and the process of refining was so conducted that their content in market products was minimized. At present the evidence at hand shows that gasolines containing up to 12 per cent of unsaturated constituents are satisfactory motor fuel, and it is generally conceded that products containing considerably more than 12 per cent of olefins can be used without trouble. Claims for the superiority of "unsatu-ated" gasolines[b] have even been made, and indications ahve been obtained in experimental work being conducted by the bureau which also point toward advantageous qualities of crcaked gasoline.

[fol. 1481] One phase of the problem of unsaturated hydrocarbons in gasoline, which is independent of commercial considerations, demands attention. In the laboratory it is frequently desirable to determine just how "unsaturated" a gasoline is, and a satisfactory laboratory method that will furnish this information is needed. The obtaining of such information will often show the source of a gasoline and tell much about its method of production.

This report does not present any radically new data, but is concerned chiefly with the correlation of existing information. Various laboratory methods were studied and experiments made. The study has dealt chiefly with methods that are frequently used without an adequate knowledge of the theoretical and experimental principles involved. The

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[a] Report of the Secretary of the Interior to the U. S. Senate; Senate Doc. 310, Feb. 2, 1916, p. 18.

[b] Hall, W. A., Address before Institution of Petroleum Technologists, London, Feb. 18, 1915. Abstracted in Petroleum World, vol. 12, March, 1915, pp. 137-149.

experimental work has dealt with the development of recognized methods to an optimum of convenience in use and with the comparison of the numerical results of the various methods.

Acknowledgments

A number of determinations of iodine numbers and percentages of sulphuric-acid absorption were made by W. A. Jacobs, of the petroleum division of the Bureau of Mines.

Krämer and Böttcher bottles were provided through the kindness of David T. Day, consulting chemist of the Bureau of Mines.

Chemistry of "Unsaturation"

A thorough discussion of the chemistry of the hydrocarbons found in petroleum and petroleum products would be too lengthy for this paper and would have no practical value, but a clear understanding of the basic principles involved is essential. For this reason the chemical properties of the various classes of petroleum hydrocarbons are briefly discussed here, but as exceptions are known to exist these statements must be understood to apply only in a general way. Only those exceptions of practical importance have been taken into account.

The comomnly accepted usage in the petroleum industry is to consider as "unsaturated" only the olefin and the acetylene hydrocarbons. The term "aromatic" is reserved for hydrocarbons of the benzene series, which, although unsaturated as regards molecular structure, differ radically from olefins in chemical activity.

[fol. 1482] The general principles upon which methods for the analysis of hydrocarbon mixtures depend are evident from the following outline of properties of the different classes of compounds:

Paraffins are of relative low specific gravity and are chemically inert.

Naphthenes are of somewhat higher specific gravity than paraffins and are chemically inert.

Olefins, including hydrocarbons having one or more double linkages between carbon atoms, have about the same specific gravity as paraffins, but are subject to various

chemical reactions; the most important of these are the addition of halogens and combination with ordinary concentrated sulphuric acid.

Acetylenes have, in addition to most of the olefin reactions, the power of combining with certain metallic salts. Acetylene hydrocarbons do not seem to occur extensively in petroleum mixtures, probably because they tend to change into aromatic hydrocarbons.

Aromatic hydrocarbons have relatively high specific gravities and occupy an intermediate position as regards chemical activity. They do not react with ordinary concentrated sulphuric acid readily, but can be made to combine with fuming sulphuric acid ("oleum"). They can be nitrated if treated under proper conditions with a mixture of nitric and sulphuric acid. Aromatic hydrocarbons can be made to combine with bromine and chlorine under properly regulated conditions, but do not take up iodine directly.

Scope of Investigation

The experiments described herein have dealt chiefly with the estimation of unsaturated constituents in mixtures that also contain paraffin or paraffin and aromatic hydrocarbons. Allowance has been made for the presence of aromatics in only the moderate proportion usual with petroleum products. The problem of estimating aromatic constituents is not considered, as none of the experiments recently performed has shown any method to be better than that described in a recent paper by Rittman, Twomey, and Egloff.*

The methods in common use for the estimation of "degree of unsaturation" have been studied in detail and data obtained that show the general relations existing among the [fol. 1483] results of these methods. The widely used "acid-heat test" proves little better than qualitative and that its results are decidedly unreliable for highly unsatu-

* Rittman, W. F., Twomey, T. J., and Egloff, Gustav: The estimation of aromatic hydrocarbons in cracked petroleum mixtures: Met. and Chem. Eng., vol. 13, October, 1915, pp. 682-686.

rated gasolines. The method of absorption by sulphuric acid and the iodine absorption method were both found to have advantages, with the balance decidedly in favor of the former. The results of either of these methods can be converted into terms of the other in a roughly approximate way, but exact agreement can not be expected, owing to differences in the mechanism of the reactions involved.

Comparison of the bromine absorption method with the iodine method showed the advantage to lie with the latter.

The work of the present investigation may be summarized as indicated in the following outline:

1. Study of experimental methods:

(a) Hanus iodine method as applied to cracked gasoline.

(b) Modifications of the method of absorption by sulphuric acid.

(c) Modifications of the Maumené test or "acid-heat test."

(d) Bromine absorption method.

2. Comparison of the results of the several methods.

Experiments

Determination of Iodine Numbers by the Hanus Method

The Hanus[a] method of determining iodine numbers seems to be the most advantageous of any yet devised for this purpose. It is more rapid than the widely used Hübl[b]

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[a] Hanus, J., Die Anwendung von Jodmonobromid bei der Analyse von Fetten und Oelen: Ztschr. Unters. Nahr. Genuss., vol. 16, 1901, pp. 913-920. Hunt, F. W., A comparison of methods used to determine the iodine values of oils: Jour. Soc. Chem. Ind., vol. 21, 1902, pp. 454-455. Smith, W. H., and Tuttle, J. B., Iodine numbers of linseed and petroleum oils: Bureau of Standards Tech. Paper 37, 1914, pp. 1-14.

[b] Hübl, —, Eine allgemein anwendbare Methode zur Untersuchung der Fette: Dingler's Poly. Jour., Bd. 253, 1884, pp. 281-295; Jour. Soc. Chem. Ind., vol. 3, 1884, pp. 641-643.

method and does not require the special reagents employed in the Wijs[c] method.

The factors of time and concentration are adequately discussed by Smith and Tuttle,[d] who recommend that a 30-[fol. 1484] minute absorption period be employed and that the quantities of Hanus solution and unknown oil be so adjusted that at the end of the reaction there remains an excess of unabsorbed iodine equivalent to 70 to 90 per cent of the quantity originally used. However, the specific recommendation regarding concentration of reagents made by these investigators for testing petroleum oils should be disregarded in favor of the more general recommendation, as their work concerned only petroleum products having a low degree of unsatuation.

Procedure Used in Experiments

Preparation of Solutions

The Hanus iodine solution is made by dissolving 13.2 grams of iodine and 3 c. c. of bromine in a liter of glacial acetic acid. This solution should be allowed to stand several days before using.

Sodium thiosulphate solution is prepared by dissolving approximately 25 grams of the crystallized salt ($Na_2S_2O_3.5H_2O$) in each liter of water.

Potassium dichromate solution is prepared by dissolving 3.8663 grams of very pure dry salt ($K_2Cr_2O_7$) in water and making up the volume to a liter. This is the basic standard solution for this method and must be prepared and preserved with great care. The quantity taken will liberate 10 grams of iodine from an acidified solution of potassium iodide.

Potassium iodide solution is made by dissolving one part by weight of the pure salt in nine parts of water.

Starch indicator solution may be prepared in various ways. The method of Gooch[e] is highly satisfactory; 5

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[c] Wijs, J. J. A., Zur Jod-Additionsmethode: Ber. Deut. Chem. Gesell., vol. 31, 1898, pp. 750-752.

[d] Smith, W. H., and Tuttle, J. B., place cited.

[e] Gooch, F. A., Methods in chemical analysis. New York, 1912, 536 pp.

grams of starch is mixed with a tiny bit (about 0.01 gram) of red mercuric iodide and rubbed to a smooth paste with cold water. This paste is poured into a liter of vigorously boiling water and stirred thoroughly, the boiling being continued for a minute or two. The solution is allowed to cool and settle; the clear portion is decanted into a bottle from which it is used. About 3 c. c. is used in each titration. If red mercuric iodide is not available the solution may be prepared without it, and when cold shaken with a few drops of chloroform, which acts as a preservative.

[fol. 1485] Standardization of Solutions

Sodium thiosulphate solution is standardized against the potassium dichromate solution as follows: 25 c. c. of the latter, equivalent to 0.25 gram of iodine, is run from a pipette into a 200-c. c. Erlenmeyer flask containing about 12 c. c. of a 10 per cent solution of potassium iodide and 5 c. c. of ordinary concentrated, chemically pure, hydrochloric acid. The iodine thus liberated is titrated with sodium thiosulphate solution, the standard of the latter being recorded in grams of iodine equivalent to each cubic centimeter of the thiosulphate solution. The thiosulphate solution needs to be restandardized occasionally, as it changes slightly on standing.

The Hanus iodine solution is standardized daily in the regular course of making determinations by "running a blank"—that is, titrating a mixture made up like one of the unknown mixtures but without any gasoline.

Method of Determination

The general scheme of procedure is as follows: Reaction mixtures are made up in the special glass-stoppered Erlenmeyer flasks sold for the purpose by chemical supply houses. The mixtures may be prepared at uniform intervals (5 minutes is a convenient period) until 30 minutes have elapsed, when the first mixture is titrated. One of the factors that insures agreement of results is uniform time of reaction, and the 30-minute period recommended by Smith and Tuttle* should not be allowed to vary more than

* Smith, W. H., and Tuttle, J. B., Iodine numbers of linseed and petroleum oils: Bureau of Standards Tech. Paper 37, 1914, pp. 1-14.

two or three minutes either way. Determinations may be run conveniently in series of six, as each mixture can be made up in a 5-minute period and the titration can be performed conveniently in that interval of time.

The procedure for a single sample is as follows: First, 10 c. c. of chloroform or carbon tetrachloride is measured into one of the glass-stoppered reaction flasks. The proper quantity of gasoline is then measured in, care being taken that there is no loss through evaporation. A convenient method of accomplishing this involves the use of a small capillary pipette made from glass tubing of about 1 mm. internal diameter and marked at intervals along its length. The volume from the pointed tip to each of the marks is [fol. 1486] determined by weighing the pipette first empty, and then filled with pure distilled water, measured at a temperature of 15° C. Different known quantities of gasoline, measured at the same temperature, can therefore be delivered from this instrument. The density of the gasoline should be known, measured for 15/15° C. The quantity used should be such that 10 to 30 per cent of the iodine used is absorbed. It is not always possible to hit on the right ratio between Hanus solution and gasoline at the first trial, but a second determination should always bring the quantities within the proper limits.

The capillary pipette, after being filled with the gasoline (at a temperature of 15° C.), is discharged with its tip held below the surface of the chloroform or carbon tetrachloride in the flask. The empty pipette is then partly washed by filling it once with the diluted gasoline mixture and letting the contents drain out. Washing is completed by filling once with pure solvent (chloroform or carbon tetrachloride) and draining again into the flask. This procedure avoids exposure of a large surface of pure gasoline to the air and reduces evaporation losses to a negligible quantity. In the present work the quantity of Hanus solution used was 10 c. c., and the quantities of gasoline between 0.04 and 0.20 gram.

The reaction mixture is allowed to stand for 30 minutes, preferably in the dark and never in direct sunlight. At the end of this time 25 c. c. of potassium iodide solution is poured in and 100 c. c. of distilled water added. The mixture is then titrated with the standardized sodium thiosulphate solution, care being taken to shake the mixture vigor-

ously as soon as the yellow color fades in the aqueous layer. This precaution is to insure the removal of the iodine dissolved in the carbon tetrachloride or chloroform layer at the bottom of the flask. The starch indicator should not be added until after the yellow color of the iodine becomes faint. Warning of the approaching end of the titration is given by the color changing from greenish to blue. The titration is complete when the blue color just fades.

The iodine number is the percentage by weight of iodine absorbed and is calculated by the following procedure: The titer of the unknown mixture is subtracted from that of a blank, consisting of Hanus solution and solvent allowed to stand 30 minutes without any gasoline, and the difference in cubic centimeters of thiosulphate solution is multiplied by the weight of iodine equivalent to each cubic [fol. 1487] centimeter of the solution. The weight of iodine thus found is divided by the weight of gasoline taken, and the quotient is multiplied by 100, which gives the iodine number.

Results of Experiments

No particular study of the details of operation of the iodine method was necessary, as the conclusions of Smith and Tuttle* served to indicate advantageous conditions of time and concentration. The device of using a capillary pipette for measuring the gasoline was all that was needed to make the Hanus iodine method practicable for use with volatile liquids. Figures for determinations of iodine numbers are given in pages 19 and 20, in connection with results of other methods of determining degrees of unsaturation.

Method of Absorption by Sulphuric Acid

The method of absorption by sulphuric acid is similar in principle to the iodine absorption method, except that it involves measurement of a decrease in the quantity of the reagent. The method is more or less widely used, but generally without a knowledge of certain devices or methods of procedure that obviate experimental difficulties. When sulphuric acid is mixed with a highly unsaturated oil or

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* Smith, W. H., and Tuttle, J. B., work cited.

gasoline there is a possibility that much heat may be developed and that gaseous reaction products may form with almost explosive violence. Some types of apparatus that are frequently used as not of proper design to minimize these difficulties and have the additional disadvantage of relatively high cost and fragility.

Discussion of Various Procedures Used in Analytical Laboratories

Two of the commonly used types of apparatus and procedure deserve discussion.

Shaking in Cylindrical Graduate

A long slender graduated cylinder with a glass stopper is often used for determining the "degree of unsaturation," the procedure being to mix equal volumes of gasoline and [fol. 1488] acid, shake the mixture, and allow it to separate by standing. The difficulties involved are considerable, as these graduates are inconvenient to handle and are inefficient in that it is difficult or even impossible to mix properly light gasoline and heavy acid in this type of container. If the reaction is violent, the contents of the tube may be completely expelled.

Use of Krämer and Böttcher Bottle

A method that has been extensively employed in one of the petroleum laboratories of the Bureau of Mines involves the use of a slender graduated tube with a flat-bottomed bulb at the bottom. This type of apparatus is described by Holde[a] in connection with the Krämer and Böttcher method for determining aromatic hydrocarbons by the sulphonation method. It is hereafter designated as the Krämer and Böttcher bottle. Equal volumes of oil and acid are measured into the bulb and are shaken thoroughly, after which enough acid is added to bring the level of the mixture nearly to the top of the graduated part of the neck. This method is accurate and fairly satisfactory if properly conducted,

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[a] Holde, D., The examination of hydrocarbon oils and of saponifiable fats and waxes; translated by E. Mueller. New York, 1915, p. 49.

but the graduated tubes are expensive, fragile, and inconvenient to handle. The single important advantage is the possibility of properly mixing oil and acid, thereby eliminating the danger of excessive heating, blowing out of the contents, and inaccurate results from incomplete absorption of the unsaturated compounds.

Use of Babcock Bottle and Centrifuge

An obviously advantageous modification of this method is the substitution of some one of the types of Babcock milk bottles for the inconvenient special graduate. Babcock bottles, on account of their extensive use, are cheap and easy to obtain, and are also of convenient size to handle. They will stand upright without support and can be placed in a centrifuge when a rapid separation of the acid and the gasoline layers is desired; their one disadvantage is that they can not be read as accurately as the Krämer and Böttcher bottles. This disadvantage is slight, however, as the degree of accuracy is sufficient for the purpose.

The use of Babcock bottles and a centrifuge for the deter- [fol. 1489] mination of unsaturated hydrocarbons is described in an article by Egloff and Twomey.[a] Their procedure was esesntially modified in the authors' experiments in one important detail, the method of mixing acid and gasoline. Egloff and Twomey recommend adding acid in small quantities to the gasoline, shaking, and cooling thoroughly after each addition. In the experiments described herein a considerable excess of acid was added rapidly to the gasoline. This procedure prevents inconvenient heating of the mixture and practically eliminates the troublesome factor of gas formation.

It is, of course, natural to expect that if the addition of a little acid to gasoline produces heat and gas, the addition of more acid will produce more heat and gas. The preceding statements to the effect that keeping the acid in excess avoids such difficulties may seem paradoxical, and the following suggestions are therefore offered in explanation of these statements. In the first place the large heat capacity of the excess acid cuts down the temperature rise. In the

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[a] Egloff, Gustav, and Twomey, T. J., The effect of temperature on the formation of olefins at atmospheric pressure: Met. and Chem. Eng., vol. 14, Mar., 1916, pp. 247-250.

second place it seems reasonable to suppose that the reaction should be considered as one in which the unsaturated hydrocarbons attack the acid rather than one in which the acid attacks the hydrocarbons. If the hydrocarbon concentration is low then the reaction is not violent and all that occurs is a combination, probably with the formation of sulphuric acid esters. If the hydrocarbons are in excess the reaction proceeds further and the acid is reduced with the formation of gaseous products such as sulphur dioxide.

Improved Method

The procedure evolved in the course of the experiments described herein is simple and has yielded satisfactory results with mixtures containing as much as 40 per cent of unsaturated hydrocarbons. The container employed is that described in the catalogues of chemical supply houses as the 6-inch, 9-gram, 40 per cent Babcock cream bottle. The neck of such a bottle is calibrated for the volume of 4.5 grams of butter fat, which is a little less than 5 c. c. An ordinary 5 c. c. pipette can be regraduated to deliver this quantity.

The gasoline to be tested is run into a clean, dry bottle, cooled for a minute or two by immersing in ice water, and [fol. 1490] then 200 per cent by volume of ordinary concentrated sulphuric acid is poured in from a small graduate. Care should be taken that the acid runs quietly down the side of the bottle, instead of splashing onto the surface of the gasoline. A rubber stopper is then placed in the bottle and the contents are shaken, first slowly, then vigorously with a rotary motion for several minutes. The gasoline and the acid are separated by either one of the following two methods.

Gravity Separation

Sulphuric acid is added to the contents of the bottle until the surface of the liquid is about level with the upper graduation mark on the neck of the bottle. The mixture is then set aside and allowed to stand overnight, when practically complete separation is effected.

Centrifugal Separation

The stoppered bottle is placed in a suitable centrifuge and revolved for two or three minutes at a speed of 500 to 1,000

r. p. m. Sufficient acid is then added to bring the level up to the lower graduation mark and the contents are again centrifuged to complete the separation. More acid is then added to bring the column to the upper graduation mark, after which the residual volume of gasoline is read.

Advantages of Method

The results obtained have a possible error of 1 to 2 per cent, but within these limits seems to be thoroughly reliable. After extensive comparison, the writers prefer this method to the iodine absorption method. The iodine method, if properly applied, is undoubtedly the more accurate, and, unless a centrifuge is available, may be considered more rapid. However, it requires the operator to have considerable skill in the technique of iodimentry and yields results that may involve large errors if operative details are wrong.

The sulphuric-acid method, on the other hand, is simple, reliable, although not highly accurate, and is more rapid than the iodimetric method if a centrifuge is available. If speed is measured in terms of the time required for the actual work of making up reaction mixtures, this method is more rapid even if overnight standing is employed, although a longer wait is then necessary before the results are available.

[fol. 1491] Comparison with Other Methods

The experiment with the sulphuric acid absorption method may be outlined under three heads, as follows:

1. Development of a convenient and rapid method of procedure and the adoption of satisfactory apparatus; study of the effect of mechanical details and comparison of various types of apparatus.

2. Comparison of results obtained with strengths of acid varying from about 88 per cent to about 95 per cent.

3. Study of possibility of interference from presence of aromatic hydrocarbons.

Effects of Apparatus and Procedure

The use of Babcock bottles and the adoption of the method of keeping acid in excess during the reaction re-

sulted from general considerations and a knowledge of the disadvantages of other types of procedure. It was, however, considered desirable to obtain experimental evidence on the agreement of results obtained by the two methods of separation—centrifugal and gravity. In addition, the results obtained with Babcock bottles and the Krämer and Böttcher bottle were compared.

The table following shows results of two series of tests, both involving the treatment of the gasoline with 200 per cent by volume of acid in Babcock bottles. In one series the acid and gasoline were separated by centrifuging three or four minutes, filling the bottle to the lower graduation mark, and again centrifuging for several minutes to complete the separation of the two layers. In the other series the mixture was allowed to stand overnight with the bottle filled to the upper graduation mark.

Comparison of Results Obtained by Centrifugal and Gravity Separation in Babcock Bottles

No. of test	Percentage absorbed by—	
	Centrifugal separation	Gravity separation
1	39	37
2	21	19
3	19	17
4	18	14
5	14	13
6	11	11
7	8	9

[fol. 1492] It is to be noted that all the differences fall within the admitted limits of error of the methods, but that there is a general tendency for results by the gravity method to be low.

The agreement between results with the Babcock centrifugal method and the method involving the use of the long-necked Krämer and Böttcher bottle is shown in the table following. The percentages of unsaturation indicated were practically identical.

Comparison of Results with the Babcock Bottle Using Centrifugal Separation, and with the Kramer and Bottcher Bottle

	First test	Second test
Absorption in Babcock bottle, per cent	39	17
Absorption in Kramer and Bottcher bottle, per cent	40	17

Effects of Variations in Strength of Acid Used

Some experiments were also made to show the effect of slight variations in the strength of the sulphuric acid used. Ordinary concentrated sulphuric acid is not always uniform, as it has a strong tendency to become diluted through absorption of moisture from the air. The table following shows results obtained when the same sample of gasoline was treated with acid mixtures of different strengths between the approximate limits of 88 per cent and 95 per cent. Two methods were employed, the Babcock centrifugal and the Krämer and Böttcher bottle method. With the former method 200 per cent by volume of acid was used, with the latter 100 per cent.

[fol. 1493] Results of Experiments Showing Slight Effect of Changing Strength of Sulphuric Acid Used Between Limits of 88 and 95 Per Cent

(One sample of gasoline was treated with various strengths of acid by two different methods.)

Acid		Percentage absorbed in Babcock bottle (centrifugal separation)		Percentage absorbed in Kramer and Bottcher bottle (gravity separation)	
Specific gravity (15°/15° C.)	Approximate acidity (percentage of H_2SO_4)	A.[a]	B.[a]	A.[a]	B.[a]
1.810	88	17	17	14.8	....
1.820	90	17	16	15.6	....
1.830	92	17	18	16.4	....
1.835	93	17	..	16.0	....
1.837	94	17	..	16.4	17.2
1.840	95	17	17	17.2	17.2

[a] Duplicate determinations.

From the figures in the above table it appears that slight variations in the strength of the acid makes no difference if 200 per cent of acid is used and do not cause considerable variations in the percentages absorbed when only 100 per cent is used.

Effects of Sulphuric Acid on Aromatic Hydrocarbons

Some experiments were performed to ascertain the effect of treating benzene, toluene, and xylene with sulphuric acid under the same conditions as the gasoline, for the purpose of ascertaining the degree to which these hydrocarbons react with ordinary concentrated sulphuric acid. The results, presented in the table following, show that benzene and toluene were practically unattacked by the acid but that about 10 per cent of the xylol[a] was absorbed. In actual fact, the total percentage that would have been absorbed if the treatment had been continued would undoubtedly have been even greater. The results show, however, that brief treatment removes only a fraction of the xylol, and as this constituent is rarely present in more than moderate proportions it is unlikely that the error introduced through its presence could exceed 1 or 2 per cent.

[fol. 1494] Results of Experiments Showing Slight Effect of Ordinary Sulphuric Acid on Aromatic Hydrocarbons

Mixture used	Per cent absorbed by Babcock bottle method		Per cent absorbed by Kramer and Bottcher method	
	A	B	A	B
25 per cent benzene and 75 per cent uncracked gasoline	1.0	1.0	...	...
10 per cent toluene and 90 per cent gasoline	1.0	1.0	0.4	0.4
100 per cent xylol	10.0	...	...	...

[a] "Xylol" is used as a convenient term for the usual mixture of isomeric xylenes.

Maumené Test or "Acid Heat Test"

A method largely used in the laboratories of refineries for determining the degree of unsaturation is the "acid heat test," which is practically identical with the Maumené[a] test, sometimes used in the testing of turpentine and fatty oils. This method really involves measuring the heat of reaction of oil and acid, conditions being regulated so that the heat of reaction is proportional to the rise in temperature.

The method is commonly applied as follows: 50 c. c. of gasoline is placed in a glass-stoppered bottle, 10 c. c. of ordinary concentrated sulphuric acid added, and the mixture shaken. The temperature is taken before the acid is added and then at intervals while the mixture is being shaken. As soon as a maximum temperature is reached the reaction is considered complete and the rise in temperature, generally expressed in Fahrenheit degrees, is called the "acid heat test" of the gasoline. "Straight" refinery gasoline generally has an acid heat test of less than 10° F. and the cracked products commonly marketed usually have tests not exceeding 30° or 40° F.

Method Is Not Suitable for Gasoline

Several details of the procedure mentioned are open to criticism, particularly as regards possible variations in the heat capacities of the containers used and the heat losses through radiation. Several other variables that might introduce errors would have been studied in the present investigation if a fundamental difficulty had not been dis- [fol. 1495] covered that makes the method essentially inaccurate for gasoline. The difficulty is simply that gasoline is such a volatile substance that part of the heat developed is dissipated in causing vaporization, instead of producing a rise in temperature. The error thus introduced is not considerable when the acid heat test is low, but with even

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[a] Maumené, M., De l'analyse des huiles au moyen de l'acide sulfurique: Compt. rend., t. 35, 1852, pp. 572-573. Leach, A. E., Food inspection and analysis, New York, 1914 3d edition, p. 494.

moderately highly unsaturated gasoline is so large as to make the results entirely unreliable.

Experiments Toward Minimizing Mechanical Source of Error

Before any experimental evidence was obtained regarding the importance of this discrepancy some experiments were performed with a view toward minimizing or obviating mechanical sources of error. It was thought in particular that the differences due to variable heat capacities of containers and losses of heat through radiation could be eliminated by using a vacuum bottle instead of an ordinary thick-walled reagent bottle. This principle was utilized by Tortelli,[a] who used a vacuum vessel and a mechanical stirrer in testing animal and vegetable oils by the Maumené reaction.

Use of Vacuum Bottle and Mechanical Stirring Compared with Use of Ordinary Bottle and Shaking

Vacuum bottles are now in such common use that they are readily obtainable and can be purchased at moderate prices. The usual metal or leather container is neither essential nor desirable, the so-called filler being all that is required. The bottles used in the experiments by the writers were of pint size and cost about a dollar apiece. A reaction vessel of this type practically eliminates losses of heat by radiation, and, owing to the thinness of the glass, is of such small heat capacity that the possibility of variation through variable heat capacity is largely reduced.

Also it was thought that more uniform results could be obtained if the acid and the gasoline were mixed with a mechanical stirrer and not by shaking. Results showing the relative merits of the shaking and the stirring methods with the vacuum bottle and of the ordinary shaking method with a plain glass bottle appear in the table following. The

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[a] Tortelli, M., Thermoleometer, Ein Apparat der gestattet Verfalschungen von Oliveöl und auch andere Pflänzen- und Tierölen zu erkennen: Chem. Centralb., Jahrg. 75, 1904, 1424-1426.

[fol. 1496] reader should note that no errors or discrepancies can increase the rise in temperature except possibly excessive stirring, and it is, therefore, obvious that the method giving the highest results is the most accurate.

Results of "Acid Heat Test" by Three Different Methods

(50 c. c. of Gasoline and 20 c. c.* of Acid Were Used in Each Test)

Sample No.	Vacuum bottle		Shaking in ordinary bottle
	Stirring	Shaking	
	°C.	°C.	°C.
1	89	83	63
2	60	61	48
3	41	53	39
4	34	38	36
5	16	30	24
6	15	26	14
7	12	11	7

The figures in the above table show that the results obtained with the vacuum bottle are always higher than those obtained with an ordinary glass bottle and that the theoretical indications of the superiority of the former are substantiated. The fortunate and convenient fact that shaking yields higher results than mechanical stirring is also shown. Each of the figures in the table represents the average of several determinations, individual figures varying over a range of 3° or 4° C.

Conclusions From Results of Experiments

To determine optimum conditions for the acid heat test, possibly a number of other variables should be studied, such as relative quantities of acid and gasoline, the strength of the acid used, and the rate of adding acid to gasoline. In the experiments described herein these factors were fixed arbitrarily, thereby eliminating possible variations from such causes, but no attempt to discover

* Twenty c. c. of acid was found to be a better quantity than 10 c. c. for gasolines of a high degree of unsaturation.

the most favorable conditions was made. The study of the acid heat test, as previously stated, was not continued because of the early discovery of the uncontrollable factor of heat losses through vaporization of the gasoline.

Conclusions with regard to the merits of the acid heat test are briefly as follows: The test is of value only for [fol. 1497] gasolines of moderately low degree of unsaturation, and when operating conditions are so maintained that the rise in temperature is proportional to the heat of reaction. The container employed should always be of a standard heat capacity and fixed quantities of acid and gasoline should be used. The strength of the acid should be always the same and the rate at which it is added to the gasoline probably should be fixed. The rating of adding acid is a particularly important source of possible variation, because the course of the reaction is probably affected by the relative concentrations of unsaturated hydrocarbons and acid. The quantity of acid used should be sufficient to react with all the unsaturated hydrocarbons, but should not be unnecessarily large, as the excess acid absorbs heat and thus cuts down the temperature rise. The use of a vacuum bottle of about one pint capacity is decidedly advantageous in that heat losses through radiation are eliminated and its heat capacity, being small, is not liable to cause important variations. Simple shaking with a rotary motion is better than the use of a mechanical stirrer.

The experiments indicate that the acid heat test is less satisfactory in operation than the method of absorption by sulphuric acid and that the results are less reliable.

Bromine Absorption Method

To supplement the study of iodine absorption, it was deemed advisable to try one of the methods involving the absorption of bromine.

Description of Experiments and Results

The method of McIlhiney[a] seemed most promising and was selected as representative. This method involves ab-

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[a] McIlhiney, P. G., The determination of bromine absorption of oils: Jour. Am. Chem. Soc., vol. 21, 1899, pp. 1084-1089.

sorption of bromine in a medium of carbon tetrachloride during a reaction period of 30 minutes. The excess of bromine is determined by adding potassium iodide solution and titrating the liberated iodine with standarized sodium thiosulphate solution. The proportion of bromine that goes to form substitution products instead of being directly added to the hydrocarbon molecules should also be determined. This is accomplished by a supplementary titration, with thiosulphate, of the iodine liberated when a [fol. 1498] neutral solution of potassium iodate is added to the reaction mixture. The true bromine addition value is found by subtracting twice the amount found by the last titration from the total quantity of bromine absorbed. The reactions involved are as follows:

1. Bromine addition (typical)—

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethyelne bromide.}}{C_2H_4Br_2}$$

2. Bromine substitution (typical)—

$$\underset{\text{Ethane.}}{C_2H_6} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethyl bromide.}}{C_2H_5Br} + \underset{\text{Hydrobromic acid.}}{HBr}$$

3. Determination of bromine substitution, which is equivalent to hydrobromic acid formation; the bromine addition value is the total bromine loss minus the sum of the equal quantities of bromine substituted and convereted into hydrobromic acid—

$$\underset{\text{Hydrobromic acid.}}{6HBr} + \underset{\text{Potassium iodate.}}{KIO_3} + \underset{\text{Potassium iodide.}}{5KI} = \underset{\text{Iodine.}}{3I_2} + \underset{\text{Potassium bromide.}}{6KBr} + \underset{\text{Water.}}{3H_2O}$$

Comparison with Iodine Method

Bromine numbers were determined by this method for a series of samples of varying degrees of unsaturation. With these samples the amount of bromine substituted proved to be practically a negligible quantity. Results of the tests

are shown in the following table. The iodine numbers, and the theoretical bromine values, calculated from the iodine numbers by multiplying by the ratio of the chemical equivalents of the two halogens, are also shown.

Experimentally Determined Bromine Numbers of a Series of Unsaturated Naphthas Compared with Bromine Numbers Calculated from Iodine Numbers Determined by the Hanus Method

Sample No.	Bromine value determined by experiment	Bromine value calculated from iodine value	Iodine No.
1	162.9	165.6	263.0
2	103.5	91.3	144.8
3	78.4	80.3	127.4
4	72.8	72.2	114.6
5	50.3	55.0	87.4
6	49.7	41.8	66.4
7	35.6	29.4	46.7

[fol. 1499] Conclusions as to Bromine Method

The agreement between the determined and the calculated bromine numbers was reasonably good, but there was more difficulty in obtaining concordant duplicate results with the bromine than with the iodine method. Also more time was consumed in making the determinations by the bromine method and there seemed to be no advantages from its use. Greater rapidity has been claimed by some operators for the bromine method, but undoubtedly on the basis of comparison with one of the slower iodine methods, as for instance, the Hübl.

Relations Between Results Obtained by the Several Methods of Measuring Degree of Unsaturation

In addition to making a study of the actual methods of determining degrees of unsaturation it was thought desirable to obtain figures showing the relations between results of the several methods.

Realtion of "Acid Heat Test" Value to Iodine Number and to Percentage of Absorption in Sulphuric Acid

The table following shows the results of "acid heat tests" of a series of samples, as compared with the iodine numbers and the percentages of absorption in sulphuric acid of these samples:

Results Showing Relation of "Acid Heat Test" Values (in Degrees Centigrade) with Iodine Numbers and with Percentages of Absorption by sulphuric Acid

Sample No.	Percentage of absorption by acid	Per cent acid absorption ÷ acid heat test	Acid heat test (°C)	Iodine number ÷ acid heat test	Iodine number
1	39	0.47	83	3.2	263
2	21	.34	61	2.4	145
3	19	.36	53	2.4	127
4	18	.47	38	3.0	115
5	14	.47	30	2.9	87
6	11	.42	26	2.5	66
7	8	(.73)	11	(4.2)	47

From the above figures it apears that the relations between the several values vary within rather wide limits. Moreover, the small number of results available for com- [fol. 1500] parison does not permit the inference that even these extremes represent the actual limits. The possibility of variations through changes in details of operation of the acid heat test render undesirable the giving of the impression that any definite relation exists between results of this test and those of the other two methods.

For purposes of rough comparison and in the absence of more comprehensive data, it may be said that the precentage of absorption in acid is between 0.3 and 0.5 times the acid heat test value expressed in degrees centigrade, in tests made by mixing 50 c. c. of gasoline and 20 c. c. of sulphuric acid in a vacuum bottle of about 1 pint capacity. The iodine number is 2 to 3.5 times the acid heat test value in tests performed in the same way. If the acid heat test value is given in degrees Fahrenheit the factor for conver-

sion into the percentage of unsaturation is between the limits of 0.16 and 0.28, and for transformation into the iodine number is between 1.1 and 1.9.

In this connection, the authors again emphasize the fact that the acid heat test, as usually determined for gasoline, is so thoroughly empirical that the figures given in the relations stated above must be considered as having only a roughly general accuracy.

Relation of Iodine Number and Percentage of Absorption by Sulphuric Acid

The relation between results of the sulphuric acid and the iodine absorption methods is more important in the present connection because a considerable number of figures are available for comparison; also the two methods are accurate enough so that no considerable variations are due to experimental error.

The values given in the previous table for percentage of acid absorption, iodine number, and ratio of the iodine number to the acid absorption of the seven samples tested are repeated in the table following, which also gives the results of a series of unsaturation measurements made by both of the two methods. These latter figures were obtained in connection with a study of the production of gasoline by the vapor-phase cracking process, the results of which will appear in a future report. The ratios found by dividing the iodine numbers by the percentages of unsaturation vary in general between the limits of 6 and 7, with occasional extremes as low as 5.3 and as high as 7.5. The average is 6.5.

[fol. 1501]

Comparison of results obtained by measuring unsaturation of gasoline by the sulphuric acid absorption and the iodine absorption method

Test No.	Percentage of acid absorption	Iodine number	Iodine number ÷ acid absorption	Test No.	Percentage of acid absorption	Iodine number	Iodine number ÷ acid absorption
1.....	39	263	6.7	23.....	39	249	6.4
2.....	21	145	6.8	24.....	32	249	7.2
3.....	19	127	6.7	25.....	31	213	6.9
4.....	18	115	6.4	26.....	26	157	6.0
5.....	14	87	6.2	27.....	26	164	6.3
6.....	11	66	6.0	28.....	29	161	5.5
7.....	8	47	5.8	29.....	26	142	5.4
8.....	46	293	6.3	30.....	23	155	6.8
9.....	38	270	7.1	31.....	25	146	5.8
10.....	41	257	6.3	32.....	23	161	7.0
11.....	32	208	6.5	33.....	22	149	6.7
12.....	34	215	6.3	34.....	16	114	7.1
13.....	33	214	6.5	35.....	20	114	5.7
14.....	32	229	7.1	36.....	18	95	5.3
15.....	31	204	6.6	37.....	17	112	6.6
16.....	31	231	7.5	38.....	14	84	6.0
17.....	30	190	6.3	39.....	13	97	7.5
18.....	31	214	6.9	40.....	16	109	6.8
19.....	31	212	6.8	41.....	20	120	6.0
20.....	37	245	6.6	42.....	16	112	7.0
21.....	39	254	6.5	43.....	20	114	5.7
22.....	37	248	6.7	Average ratio.....			6.5

Probably the failure to attain closer constancy in the various determinations of the ratio is not wholly due to experimental error, for there are fundamental differences in the chemical mechanism of the two reactions. Absorption by sulphuric acid is a measure of the number of hydrocarbon molecules having one or more unsaturated linkages. Iodine absorption measures the actual number of such linkages, whether single or several, in each molecule.

Approximate Ratio for Converting Iodine Number to Percentage of Unsaturation

From the evidence at hand it appears that for gasoline the ratio 6.5 can safely be used for approximate conversion of percentages of unsaturation into iodine numbers. For some cracked distillate oils, studied in another connection, the ratio was slightly lower, and for cracked residuum oils was considerably lower, indicating that more material was

attacked by acid than by iodine. This variation is to be expected, for asphaltic material is removed by acid in common refining practice. It therefore appears that the use [fol. 1502] of the ratio of 6.5 generally should be limited to tests of gasoline and should never be employed for oils containing appreciable quantities of pitchy material.

Ratio for Converting Bromine and Iodine Numbers

Bromine numbers can be approximately converted into iodine numbers by multiplying the bromine number by the ratio of the chemical equivalents of the two halogens, which is $\frac{126.9}{79.9}$, or 1.59.

Summary

A study of the analytical methods for estimating unsaturated hydrocarbons, characteristic products of the cracking reaction, in gasoline gave these results:

The Hanus iodine method, if properly applied, is satisfactory for estimating the degree of unsaturation of gasoline. Determinations can be made with moderate rapidity and the results are accurate. The method, however, requires much care and some skill in the technique of iodimetry.

The sulphuric acid absorption method is rapid, reliable, and of fair accuracy. Its value depends on the use of convenient apparatus and the observance of simple but necessary precautions in the details of manipulation. This method, as employed in the experiments described in this report, is highly recommended as satisfactory for general use.

The "acid heat test" (determination of Maumené numbers) proved unreliable, especially for highly unsaturated mixtures. Primary objections are the many empirical factors involved and the dissipation of much of the heat in volatilizing gasoline instead of producing a rise in temperature. Experiments showed that the acid heat test could be made most accurately by using as a container a vacuum bottle of about 1-pint capacity, and mixing the oil and acid by hard shaking.

The bromine absorption method proved less desirable than the iodine method, although giving approximately equivalent results.

By comparing the three methods—iodine absorption, sulphuric acid absorption, and "acid heat test"—ratios were found for transforming each set of values into terms of the other. These ratios as applied to the "acid heat test" are only rough approximations. The ratio for transforming [fol. 1503] iodine numbers into terms of percentage of sulphuric acid absorption is not essentially a constant, but for cracked gasolines varies between fairly close limits. The average figure is 6.5, and most of the values fall within the limits of 6 and 7.

Publications on Petroleum Technology

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Publications Available for Free Distribution

Bulletin 120. Extraction of gasoline from natural gas by absorption methods, by G. A. Burrell, P. M. Biddison, and G. G. Oberfell. 1917. 71 pp., 2 pls., 15 figs.

Bulletin 134. The use of mud-laden fluid in oil and gas wells, by J. O. Lewis and W. F. McMurray. 1916. 86 pp., 3 pls., 18 figs.

Bulletin 148. Methods for increasing the recovery of oil from wells, by J. O. Lewis. 1917. In press.

Technical Paper 32. The cementing process of excluding water from oil wells, as practiced in California, by Ralph Arnold and V. R. Garfias. 1913. 12 pp., 1 fig.

Technical Paper 37. Heavy oil as fuel for internal-combustion engines, by I. C. Allen. 1913. 36 pp.

Technical Paper 38. Wastes in the production and utilization of natural gas, and methods for their prevention, by Ralph Arnold and F. G. Clapp. 1913. 29 pp.

Technical Paper 42. The prevention of waste of oil and gas from flowing wells in California, with a discussion of special methods used by J. A. Pollard, by Ralph Arnold and V. R. Garfias. 1913. 15 pp., 2 pls., 4 figs.

Technical Paper 45. Waste of oil and gas in the Mid-[fol. 1504] Continent fields, by R. S. Blatchley. 1914. 54 pp., 2 pls., 15 figs.

Technical Paper 66. Mud-laden fluid applied to well drilling, by J. A. Pollard and A. G. Heggem. 1914. 21 pp., 12 figs.

Technical Paper 68. Drilling wells in Oklahoma by the mud-laden fluid method, by A. G. Heggem and J. A. Pollard. 1914. 27 pp., 5 figs.

Technical Paper 70. Methods of oil recovery in California, by Ralph Arnold and V. R. Garfias. 1914. 57 pp., 7 figs.

Technical Paper 72. Problems of the petroleum industry, results of conferences at Pittsburgh, Pa., August 1 and September 10, 1913, by I. C. Allen. 1914. 20 pp.

Technical Paper 79. Electric lights for oil and gas wells, by H. H. Clark. 1914. 8 pp.

Technical Paper 87. Methods of testing natural gas for gasoline content, by G. A. Burrell and G. W. Jones. 1916. 26 pp., 7 figs.

Technical Paper 104. Analysis of natural gas and illuminating gas by fractional distillation in a vacuum at low temperatures and pressures, by G. A. Burrell, F. M. Seibert, and I. W. Robertson. 1915. 41 pp., 7 figs.

Technical Paper 117. Quantity of gasoline necessary to produce explosive vapors in sewers, by G. A. Burrell and H. T. Boyd. 1916. 18 pp., 4 figs.

Technical Paper 127. Hazards in handling gasoline, by G. A. Berrell. 1915. 12 pp.

Technical Paper 130. Underground wastes in oil and gas fields and methods of prevention, by W. F. McMurray and J. O. Lewis. 1916. 28 pp., 1 pl., 8 figs.

Technical Paper 131. The compressibility of natural gas at high pressures by G. A. Burrell and I. W. Robertson. 1916. 11 pp., 2 figs.

Technical Paper 161. Construction and operation of a single-tube cracking furnace for making gasoline, by C. P. Bowie. 1916. 16 pp., 10 pls.

Technical Paper 163. Physical and chemical properties of gasolines sold throughout the United States during the calendar year 1915, by W. F. Rittman, W. A. Jacobs, and E. W. Dean. 1916. 45 pp., 4 figs.

[fol. 1505] Publications That May Be Obtained Only Through the Superintendent of Documents

Bulletin 19. Physical and chemical properties of the petroleum of the San Joaquin Valley, Cal., by I. C. Allen and W. A. Jacobs, with a chapter on analyses of natural gas from the Southern California oil fields, by G. A. Burrell. 1911. 60 pp., 2 pls., 10 figs. 10 cents.

Bulletin 32. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 38 pp. 5 cents.

Bulletin 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion engines, by R. M. Strong and Lauson Stone. 1912. 243 pp., 3 pls., 32 figs. 20 cents.

Bulletin 65. Oil and gas wells through workable coal beds; papers and discussions, by G. S. Rice, O. P. Hood, and others. 1913. 101 pp., 1 pl., 11 figs. 10 cents.

Bulletin 88. The condensation of gasoline from natural gas, by G. A. Burrell, F. M. Seibert, and G. G. Oberfell. 1915. 106 pp., 6 pls., 18 figs. 15 cents.

Bulletin 114. Manufacture of gasoline and benzene-toluene from petroleum and other hydrocarbons, by W. F. Rittman, C. B. Dutton, and E. W. Dean, with a bibliography compiled by M. S. Howard. 1916. 268 pp., 9 pls., 45 figs. 35 cents.

Bulletin 125. The analytical distillation of petroleum, by W. F. Rittman and E. W. Dean. 1916. 79 pp., 1 pl., 16 figs. 15 cents.

Technical Paper 3. Specifications for the purchase of fuel oil for the Govferences at Pittsburgh, Pa., August 1

and September 10, 1913, by I. C. Allen. 1911. 13 pp. 5 cents.

Technical Paper 10. Liquefied products of natural gas, their properties and uses, by I. C. Allen and G. A. Burrell. 1912. 23 pp. 5 cents.

Technical Paper 25. Methods for the determination of water in petroluem and its products, by I. C. Allen and W. A. Jacobs. 1912. 13 pp., 2 figs. 5 cents.

Technical Paper 26. Methods for the determination of the sulphur content of fuels, especially petroluem products, by I. C. Allen and I. W. Robertson. 1912. 13 pp., 1 fig. 5 cents.

Technical Paper 36. The preparation of specifications for petroleum products, by I. C. Allen. 1913. 12 pp. 5 cents.

Technical Paper 51. Possible causes of the decline of [fol. 1506] oil wells, and suggested methods of prolonging yield, by L. G. Huntley. 1913. 32 pp., 9 figs. 5 cents.

Technical Paper 53. Proposed regulations for the drilling of oil and gas wells, with comments thereon, by O. P. Hood and A. G. Heggem. 1913. 28 pp., 2 figs. 5 cents.

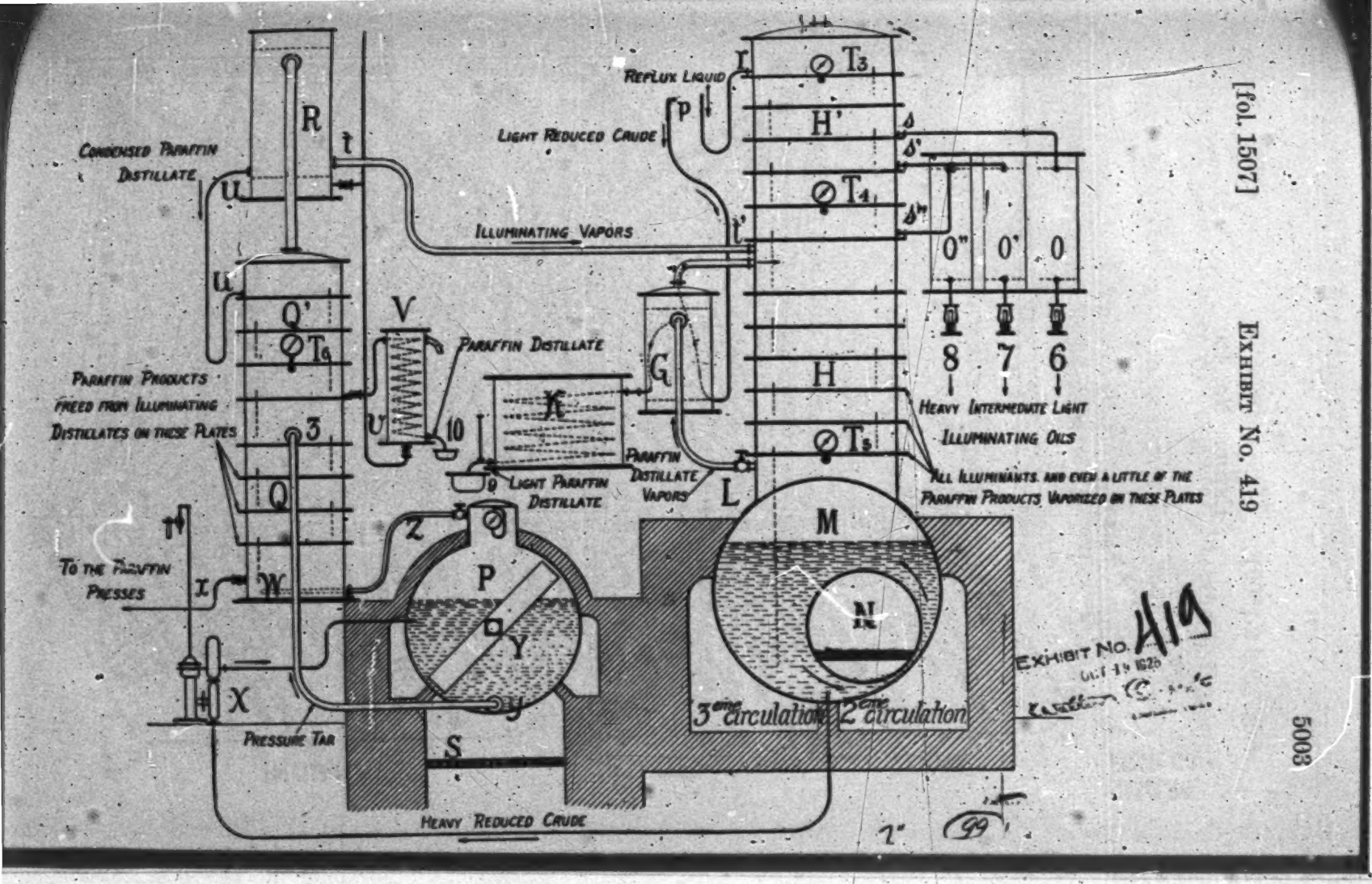
Technical Paper 57. A preliminary report on the utilization of petroleum and natural gas in Wyoming, by W. R. Calvert, with a discussion of the suitability of natural gas for making gasoline, by G. A. Burrell. 1913. 23 pp. 5 cents.

Technical Paper 74. Physical and chemical properties of the petroleums of California, by I. C. Allen, W. A. Jacobs, A. S. Crossfield, and R. R. Matthews. 1914. 38 pp., 1 fig. 5 cents.

Technical Paper 109. Composition of the natural gas used in 25 cities, with a discussion of the properties of natural gas, by G. A. Burrell and G. G. Oberfell. 1915. 22 pp. 5 cents.

Technical Paper 115. Inflammability of mixtures of gasoline vapor and air, by G. A. Burrell and H. T. Boyd. 1915. 18 pp., 2 figs. 5 cents.

Technical Paper 120. A bibliography of the chemistry of gas manufacture, by W. F. Rittman and M. C. Whittaker, complied and arranged by M. S. Howard. 1915. 30 pp. 5 cents.



[fol. 1507]

Exhibit No. 419

EXHIBIT NO. 419
Oct 14 1926

5003

[fols. 1508 & 1509]

EXHIBIT No. 420

[fol. 1510] EXHIBIT No. 471

Oct. 20, 1926. Walter N. Carpenter, Shorthand Reporter

Outlines of Industrial Chemistry, a Text-book for Students

By Frank Hall Thorp, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology

New Edition, Revised

New York: The Macmillan Company. London: Macmillan & Co., Ltd. 1899

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known as "cracking,"* by which the yield of these is increased, has come into general use in recent years. As has already been shown, the upper part of the still is exposed to the air and thus cooled. When the heavy oils begin to distill, the fire is so modified that only the bottom of the still is heated very hot, while the top and sides cool somewhat. Thus the heavy-oil vapors are condensed within the still itself, and drop back into the residuum, which, being much hotter than the boiling point of the oil, causes a breaking up of the oils of high molecular weight into lighter oils of less molecular weight and lower boiling points, while some carbon separates, forming a coke on the bottom of the still. This deposit of carbon must be removed at frequent intervals.

The reactions which occur in "cracking" are probably complex. The heavy oils are decomposed into paraffines and olefines of lower boiling points, and very probably hydrocarbons of the aromatic and methylene series are also produced. The number of products is doubtless quite large. As examples of what may, perhaps, take place, the following may be assumed: the hydrocarbon, $C_{18}H_{38}$ (octa-[fol. 1511] decane), boiling at 317° C., might decompose into $C_{10}H_{22}$ (decane), boiling at 173°, and C_7H_{16} (heptane), boiling at 98° C., and carbon. Or it might form a paraffine

* The history of the discovery of this process is given in chap. iii of Petroleum Distillation, by A. N. Leet, New York, 1884.

and an olefine, e. g. C_8H_{18} (octane), boiling at 125° C., and $C_{10}H_{20}$ (decylene), boiling at 172° C. The lower boiling product would be put with the naphtha distillate, and the higher boiling would form a part of the burning oil.

The several distillates obtained from the crude oil are redistilled and divided into further subdivisions.

The benzine distillate yields†:—

Cymogene	B. P. = 32° F.	Sp. Gr. = 0.590—0.610	Petroleum Ether
Rhigolene,	B. P. = 60° F.	Sp. Gr. = 0.625—0.631	Petroleum Ether
Gasoline,	B. P. = 115° F.	Sp. Gr. = 0.635—0.666	Petroleum Ether
C Naphtha (Benzine)	B. P. = 122°—140° F.	Sp. Gr. = 0.678—0.700	
B Naphtha,		Sp. Gr. = 0.714—0.718	
A Naphtha (Petroleum naphtha),		Sp. Gr. = 0.741—0.745	

The burning oil distillate yields:

110° fire test burning oil ("Standard white").	Export Oil.
120° fire test burning oil ("Prime white").	Export Oil.
150° fire test burning oil ("Water white").	Export Oil.

The residuum from the above distillation is transferred to the tar still, or if the distillation has been carried on under vacuum, it is known as "reduced oil," and is used to make fine lubricating oils or vaseline.

The tar stills are cylindrical, and are set in much the same way as those already described, but are encased in brickwork almost to the top. They are provided with pipes for introducing superheated steam, and are much smaller than the crude oil stills.

The first distillate is collected until the gravity is about 38° Bé. (0.834 sp. gr.), and is mixed with the next charge of crude oil, or washed with acid and soda and refined for burning oil. Then follow several distillates of increasing color and density, which are purified as described below, and treated to separate the paraffine wax and lubricating oils. The distillation is carried on until the still bottom is red-hot, when a gummy yellow distillate, called "yellow wax," is collected. This contains anthracene and other hydrocarbons of high molecular weight. The residue of coke is highly valued for electric light carbons and other electrical purposes.

The fractions collected from the burning oil distillate are more or less yellow, colored by tarry matters, which

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†Boverton Redwood—Groves and Thorp's Chemical Technology, Vol. II.

would collect in the lamp-wick and soon choke it. To re- [fol. 1512] move these impurities, the oil is put into an "agitator," a large, lead-lined, iron tank, where it is mixed with from 1 to 2 per cent of concentrated sulphuric acid, and the mixture stirred by blowing in air at the bottom. The acid unites with the tarry matters, and when the blast is stopped, sinks to the bottom and is drawn off as "sludge acid." Water is added, and after the mixture is agitated, is drawn off. Next a solution of caustic soda is introduced (about 1 per cent), and the contents of the tank again agitated. Then the oil is again washed with water and drawn into the settling tanks, where the suspended water settles out, leaving a bright, clear oil. These tanks are very shallow, usually only about 1 foot or 15 inches deep, but may cover an area of 20 by 30 feet. They are exposed to the light and air, and usually contain steam coils for warming the oil in winter.

If the oil is now found to have too low a flash point (p. 295), it is run through a "sprayer," an upright pipe with cross-arms of small perforated pipe, through which the oil is forced into the air in fine jets or spray; after falling some distance, it is collected in tanks. By this exposure to air, any light oils, such as benzine or naphtha, are volatilized, and the flash point thus raised. But spraying is less frequently necessary now, since more care is taken in the original distilling.

[fol. 1513] EXHIBIT No. 472

A HANDBOOK
OF THE
PETROLEUM INDUSTRY

BY

DAVID T. DAY, Ph.D.
EDITOR-IN-CHIEF

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IN TWO VOLUMES

OCT 26 1926
EXHIBIT No. 472
26 1926

NEW YORK
JOHN WILEY & SONS, INC.
LONDON: CHAPMAN & HALL, LIMITED
1922

No practical application of cracking was introduced until four years after its discovery. During this interval various experiments were made, with the result that in 1865 patents were issued to Young and Benton. Young's process was conducted in the liquid phase in a still designed to effect condensation on the upper portions with the consequent dropping back of the condensed particles into the boiling liquid, thus causing dissociation.

Young proposed the use of pressure of from 10 to 20 pounds per square inch and aimed at the production of lamp oils and kerosene from Scottish shale oils.

The process of Benton followed that of Young, and was also conducted in the liquid phase. It was the first attempt to utilize tubes for cracking purposes. Benton provided

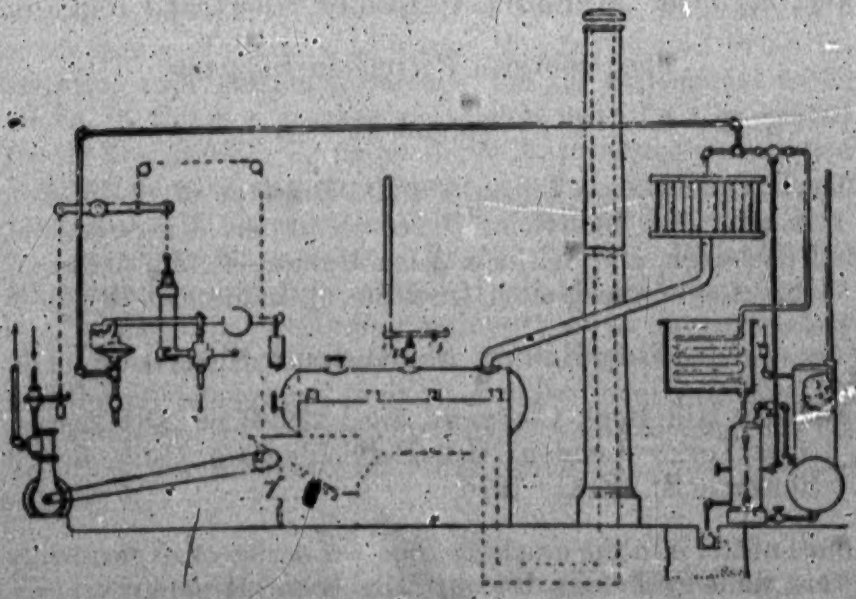

FIG. 2.—The Humphrey and Burton process. It produces more motor spirit than any thus far developed

for a temperature ranging from 357° to 538° C. under a pressure of 500 pounds per square inch or less.

Others of the more important early patents were those issued to A. Reibeck's Mining Works and to J. Dewar and B. Redwood about 1890.

The last-named patent covered a process conducted in a still under pressure and designed for the production of lamp oils or kerosene. The experiments were made in Russia. Due to the production of comparatively large quantities of gasoline, which was practically unsalable at that time, the process was abandoned. This process resembled very closely the well-known Burton process, the principal difference being the emphasis that Burton placed upon condensation under pressure. Great credit is due to Dewar and Redwood for having produced so efficient an apparatus at such an early date.

[fol. 1515] EXHIBIT No. 473

Oct. 26, 1926. Walter N. Carpenter, Shorthand Reporter

The American Petroleum Industry

Volume II

By Raymond Foss Bacon, Ph. D., Director of the Mellon Institute of Industrial Research of the University of Pittsburgh, and William Allen Hamor, M. A., Assistant Director of the Mellon Institute of Industrial Research

First Edition, Fourth Impression

McGraw-Hill Book Company, Inc., 239 West 39th Street, New York. London: Hill Publishing Co., Ltd., 6 & 8 Bouverie St., E. C. 1916

duce nickel into the cracking zone. A series of experiments were made by Brooks, Bacon, Padgett and Humphrey, at atmospheric pressure and at temperatures of 500-550° C., employing various catalytic substances. Kerosene and solar oil vapors passed through an iron tube containing burned clay, carbon, coarse and finely divided iron, coarse and finely divided copper, heated to the above-named temperature, yielded gasoline fractions, which showed an olefine content of approximately 25 to 30 per cent. When nickel was employed, the per cent of olefines in the gasoline product was 48 per cent.

The effect of nickel in increasing the per cent of olefines, when operating at atmospheric pressure, opens up the question of the effect of foreign substances on the polymerization of olefines and the effect thereon of different physical factors. The percentage of olefines indicated in the above figure does not represent the minimum obtainable even without the addition of a "catalyst."

[fol. 1516] The claim is made by Burton[1] that by placing the pressure-controlling valve beyond the condenser so as to condense the volatile gasoline vapors produced by distilling heavy petroleum oils under about 75 lb. pressure, olefines are not produced; whereas, if the pressure controlling valve is placed between the still and condenser, olefines are found in the condensate to such an extent as to render the latter process of doubtful commercial utility. Brooks and his co-workers felt that if olefines could somehow be squeezed together or polymerized by 75 lb. pressure in a condenser containing cold water, this fact would be an interesting contribution to science; but the experiment noted above, in which a cracked petroleum naphtha was heated for 30 hr. at 196° C., under 3,000 lb. pressure per square inch practically without change (iodine number reduced from 55.0 to 52.9), seemed to render such a reaction as Burton describes improbable. Brooks, Bacon, Padgett and Humphrey accordingly prepared several gallons of gasoline by distilling Oklahoma "reduced" oil at approximately 80 lb. pressure, in one case with the valve between the still and the condenser, and in another experiment with the still and condenser in free communication, so as to condense the vapors under pressure, all other conditions remaining the same.

Gasoline

Per cent. refining loss by 5 per cent. conc. H_2SO_4	7.9	8.0
Per cent. refining loss by 5 per cent. "oleum"	12.2	12.0

Kerosene, boiling point 302-392° F.

Per cent. refining loss by 5 per cent. "oleum"	12.2	12.0

In I the valve was interposed between the still and condenser; and in II the still and condenser were in free com-

[1] United States Patent 1049667. Under Int. Conv., July 3, 1912. The Burton process is described on p. 573.

munication, the control valve being beyond the condenser. These results seem to verify the opinion expressed above.

Dewar and Redwood[1] specified clearly that they condensed the distillate, obtained in their process, under pressure. In United States Patent 726,173, they make the statement: "For this purpose we arrange a suitable boiler or retort and a condenser in free communication with one another, without interposing any valve between them; but we provide a regulated outlet for condensed liquid from [fol. 1517] the condenser." Aside from the above noted discovery as claimed by Burton, it is difficult to find any novelty in his patent. The operating pressures specified by Burton are 4 to 5 atmospheres. Boleg[2] described distillation under 4 atmospheres pressure, and in 1886 Krey[3] published the results obtained by distilling various crude oils, heavy oils and residues under pressures of 3 to 6 atmospheres. Engler[4] confirmed the claims of Krey, but, like Dewar and Redwood, Engler and Krey did not discover the remarkable effect of the position of the pressure-controlling valve, as referred to above.

It has been pointed out that the results presented in Fig. 197 do not represent the maximum yields of gasoline or the minimum percentage of olefines obtainable in the gasoline distillates made by distilling under pressure. Brooks, Bacon, Padgett and Humphrey did not point out the optimum working conditions of the process. However, in the patent of Bacon, Brooks and Clark[5] it has been shown that the ratio between the volume of the oil heated and the area of the heating surface of the apparatus employed is an important factor. This relation may perhaps be more clearly understood if it is stated that, other conditions remaining the same, cracking does not occur throughout the mass.

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[1] *Loc. cit.*
[2] Chem. Rev. Fett-Harz-Ind., 9 (1898), 24.
[3] German Patent 37728, 1886.
[4] Ber., 30 (1897), 2919.
[5] United States Patent 1131309, Mar. 9, 1915.

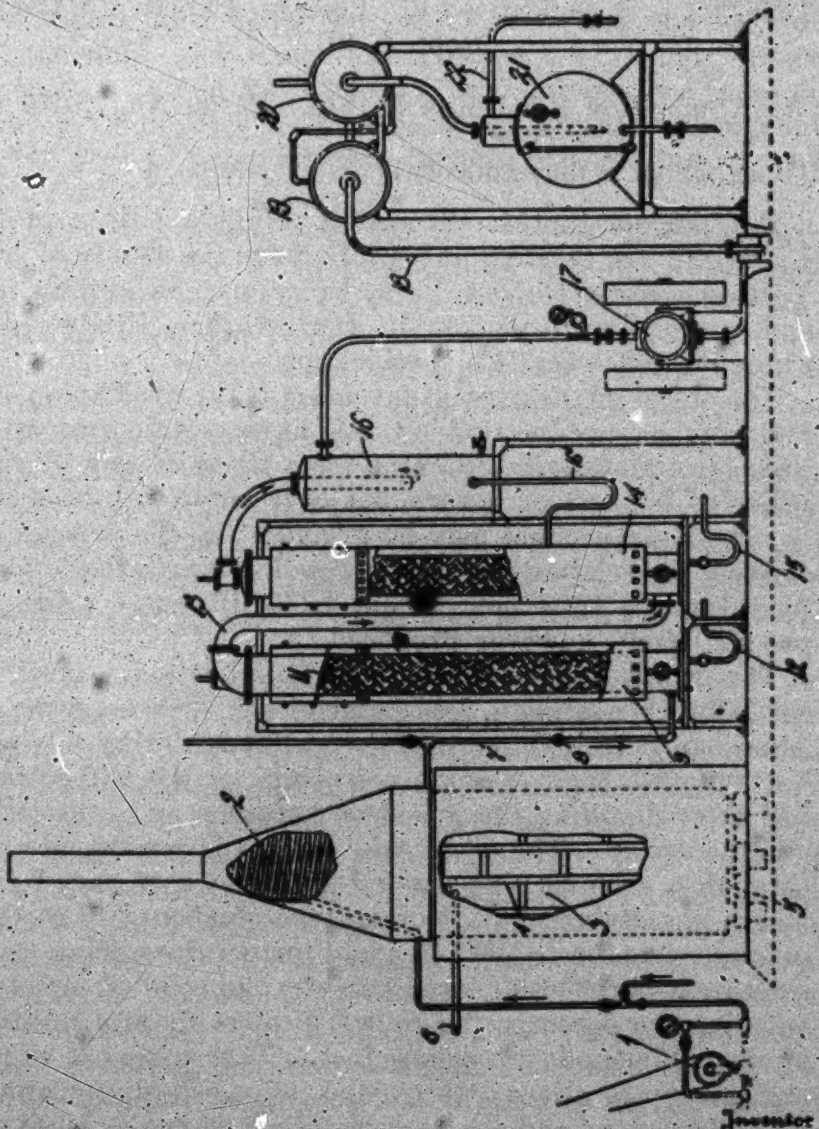
[fol. 1518] EXHIBIT No. 511

W. A. HALL.

HYDROCARBON PRODUCT.

APPLICATION FILED MAY 7, 1915.

1,239,099. Patented Sept. 4, 1917.



Witnesses

Inventor

William A. Hall

By A. B. Foster

Witness

[fol. 1519] United States Patent Office

William Augustus Hall, of New York, N. Y.

Hydrocarbon Product

1,239,099. Specification of Letters Patent. Patented Sept. 4, 1917

Application Filed May 7, 1915. Serial No. 26,546

To all whom it may concern:

Be it known that I, William A. Hall, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Hydrocarbon Products, of which the following is a specification.

The object of the present invention is the production of a hydrocarbon product, which will have certain properties which are materially different from those of any product which so far as I am aware, has ever heretofore been produced. Said product may be produced by the process described and claimed in my copending application 3,955, filed Jan. 23, 1915, now Patent 1,175,910, but I claim the product itself, however produced.

The process, as described in said application consists essentially, in heating a hydrocarbon oil, such as solar oil, American petroliate, or kerosene, although other oils may be employed, such as crude petroleum, or the still bottoms left after distilling the gasolene, kerosene and lubricating oils therefrom. The oil in said process is passed into and through a tube or pipe, having a diameter of say, 1 to 3 inches, maintained at a temperature of about 540 to 600° or more, even up to 700° C., (said temperature being measured by a pyrometer placed between the coils of pipe constituting the decomposing retort) preferably at a pressure of about 75 pounds per square inch. Thereafter the vapors and gases are allowed to expand, to substantially atmospheric pressure, and are conveyed through one or more air-cooled receptacles or towers filled with a checker work of broken pottery or the like, in order to allow the temperature to fall to about 180 or 200° C., or even down to 100° C. In these receptacles or towers, the major portion of

the undecomposed heavy oils, free carbon, and vaporized materials of which the boiling point is much above the temperature stated, are separated from the remaining gases and vapors. The gases and vapors together with any mist of fine liquid particles carried thereby, are then subjected to a considerable pressure, a pressure of 100 to 125 pounds per square inch being suitable, and during the step of compression, the temperature, instead of rising, drops somewhat, (about 15 or 20 degrees C., or in some cases as much as 38 degrees C., or more, being the observed amount of the drop in temperature in certain experiments which I have made).

The crude product, produced in accordance with this process, for example in experiments 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, described below, has a more or less disagreeable, varnish-like odor, and contains a material dissolved therein which is of a yellow color, and a resinous collodial nature. When the fuel evaporates, this remains as a dark-orange, non-drying resinous substance, with a varnish-like odor. This can be removed from the fuel, together with the color of the fuel, by distilling with fullers' earth, or by filtering through the same, or by treatment with sulfuric acid and distilling, or by other appropriate methods. This resinous material may be recovered as a by-product, for use in the arts.

Experiment 1: A gas oil having a specific gravity of .86 was used, the temperature — the decomposing coils was about 600° — (external, corresponding to a somewhat lower temperature internal, which would necessarily vary more or less between the upper and lower bends of the pipe and would also vary more or less according to the speed of flow) a pressure in the decomposing coils of 75 pounds per square inch, a temperature at the inlet of the compressor of about 180° C., and a pressure at the outlet of the compressor of 125 pounds per square inch. The product before clarifying, had a disagreeable, varnish-like odor. After distilling, the product is found to consist of a hydrocarbon product, having certain properties as follows:—It has an initial boiling point as low as or lower than ordinary gasolene, and has larger fractions volatile below a temperature of 80° C., than ordinary gasolene. It is substantially free from liability to pre-ignite, and therefore when used as a motor fuel in an ordinary automobile engine "knock-

ing" does not occur, even with the spark advanced. The absence of knocking will obviously produce much less wear and tear on the engine, than would be produced with ordinary gasolene. The mixture of air and the fuel ignites very readily, but the flame does not propagate itself through the mixture of air and vapors as rapidly as with [fol. 1520] ordinary gasolene. In other words it is slow-burning, hence its freedom from "knocking." On account of the high percentage of low volatile contents, it can be cut at 180° C., or higher, as compared with 160° C., in ordinary gasoline.

Its larger fractions volatile at low temperature have been found to carry complete combustion to the fractions volatile only at the highest temperatures, a considerably increased mileage per gallon consumed being the result.

The low flash point and low initial boiling point give in an engine run on the fuel, great ease in starting in cold weather, and owing to its large fractions volatile at low temperatures, great flexibility (quickness of acceleration) is obtained. It has been found that as great flexibility and ease of starting can be obtained with this fuel when "cut" at 180° C. and of specific gravity 0.760 as can be obtained with a straight gasolene of specific gravity 0.730 "cut" at 160° C.

A distinguishing characteristic of the new fuel is that it contains a proportion of unsaturated hydrocarbons which proportion will naturally vary with the oil used in its production, and with the conditions of operation of the process. It contains a large percentage of hydrocarbons of the ethylene series but is nevertheless quite free from the objectionable features ordinarily inherent in products containing more than a small percentage of hydrocarbons of this series.

The fuel having these peculiar and highly valuable properties is the direct result of an endothermic chemical reaction between a gas which would be permanent under ordinary conditions of temperature and pressure, and a vapor of a hydrocarbon spirit which vapor if condensed to a liquid in the customary manner at atmospheric temperature, would not answer the purpose of a satisfactory motor fuel, the combination of the permanent gas and vapor being effected by mechanical compression at a temperature suffi-

ciently high to maintain the spirit portion under treatment largely or wholly in the state of vapor.

Experiment 2: The oil fed into the apparatus was that known as "Crown Diamond." The converter temperature was 685° C. (external); pressure in converter was 80 pounds per square inch; temperature at a point near the outlet of the last separator before the compressor was 130° C., pressure at the inlet of the compressor was 8 pounds, and at the outlet of the compressor was 110 pounds. The temperatures at the inlet and outlet, at intervals during the test were as follows:

Temp. at inlet of compressor	At outlet
80° C.	79° C.
82	82
84	80
84	83
86	85
87	82
90	87
90	87
91	87

In this experiment, the gases and vapors from the last separator were divided into two parts, one part passing directly through a condenser, and the other part passing through the compressor and its condenser. The liquids obtained in the two condensers were then fractionally distilled, up to 240° C., with the following results, "A" being the sample obtained by cooling only, and "B" being the sample obtained by compression and cooling:

		A	B
Total distillate up to	50° C.	.5%	5
	60	2	9
	100	18	.30
	150	54	57
	180	78	72
	200	88	81
	220	93	88
	240	96	92
Specific gravity of entire sample		.782	.740
Bromin number of fractions distilling up to	100° C.	123	145

These figures clearly show that the product obtained by compression of the heated gases and vapors is quite a different material from that obtained by cooling only.

Experiment 3: Treating by the manner substantially as above, "Crown Diamond" oil, the following figures were obtained as temperatures and pressures.

Time	Converter		Cut temperature	Compressor temperature			Compressor pressure, pounds square inch	
	Temperature	Pressure		Before	After	Difference	Before	After
	° C.		° C.	° C.	° C.	° C.		
10.55	625	75	135	106	82	24	—4	125
11.03	625	75	135	106	82	24	—4	125
11.—	625	75	136	106	83	23	—4	125
11.—	625	75	136	94	79	15	—5.5	125
11.—	625	75	135	92	75	17	—5	125
11.—	625	75	136	91	77	14	—5.5	125
11.48	625	75	136	89	74	15	—5.5	125
12.03	625	75	136	92	74	18	—5	125
12.18	625	75	136	95	74	21	—5	125
12.25	625	75	139	95	74	21	—5	125

[fol. 1521] In this experiment, the gases and vapors from the last separator were divided, a part (A) going to one condenser cooled to 0° C., and a part (B) going to the compressor and its condenser. The fractionation and other figures for the two condensates are as follows:

	A	B
First drop of condensate	31° C.	30° C.
Total condensate up to—		
50° C.	1%	2%
60	2	5
80	6	15
100	14	23
150	50	48
160	57	60
Specific gravity at 15° C.	.769	.755
Fraction boiling up to 100° C.:		
Bromin number	132.4	150.3
Iodin "	236.4	256.1
H_2SO_4 absorption	68	76

Considering that there was about 50% more liquid boiling below 100° C. in the product produced after the compression, these numbers point to the presence of an increased quantity of unsaturated products therein. It is exactly these bodies which are formed with the greatest absorption of heat—especially compounds of the acetylene series.

Experiment 4: The temperature of the converted or decomposing retort was kept at 695° C. with a pressure in the converter of 70 lbs. The temperature of the last separator before the compressor was 130° C. The compressor inlet showed —11 inches of mercury, and the outlet 100 lbs. pressure. The temperature at the inlet and outlet of the compressor at intervals during the test run was as follows:

Inlet	Outlet
98° C.	74° C.
95	75
92	76
90	77
92	76

The oil used was Crown Diamond. A connection was made at the inlet of the compressor with a copper coil for condensing, this was placed in a jacket and a water bath kept at the temperature of the inlet of the compressor, namely 93° C. and all liquid condensing at that temperature — collected (sample A.) The same arrangements were made directly after the compressor and the water bath kept at the average temperature of the outlet, namely 75° C., and the condensate collected (Sample B). All gas and vapor not condensing at this temperature was allowed to escape. A fractionation of these two samples gave results as follows:

Total distillate up to—	A	B
50° C.	½%	½%
60	1%	1%
100	6%	13%
150	32%	50%
180	65%	75%
200	83%	85%
220	93%	93%
250	98%	96%
Specific gravity	.790	.780
Boiling point (first drop)	37° C.	35° C.
Total bromin	56	63

It is interesting to note that although all the very light fractions of the spirit were allowed to escape because of the high condensing temperature employed, yet there was a difference of over 100% in the amount volatile at 100° C., in the fuel obtained when using the compressor.

Experiment 5: The converter was run at 685°C., converter pressure, 80 lbs. Temperature of last separator 130° C. The pressure gage at the inlet of compressor showed —8 inches of mercury and the outlet 110 lbs pressure. At the inlet of the compressor the gases and vapors were divided, as above, one part passing to a copper coil condensing tube as mentioned in the previous test, but cold water was used to condense all vapor coming into the coil and to cool all liquid which appeared, (liquid A). The remaining gases and vapors passed into the compressor and were compressed and cooled in the regular cooling coil and receiving

tank, (liquid B). The temperature at the inlet and outlet of compressor during the test was as follows:

Temperature	inlet	compr.	80° C.	Temperature	outlet	compr.	79° C.
"	"	"	82	"	"	"	82
"	"	"	84	"	"	"	80
"	"	"	84	"	"	"	83
"	"	"	86	"	"	"	85
"	"	"	87	"	"	"	82
"	"	"	90	"	"	"	87
"	"	"	90	"	"	"	87
"	"	"	91	"	"	"	87

The oil used in this test was Crown Diamond. A fractionation of the two samples shows as follows:

Fractionation up to—	Liquid A	Liquid B
50° C.	½%	5%
60	2%	9%
100	18%	30%
150	54%	57%
180	78%	72%
200	88%	81%
220	93%	88%
240	96%	92%
Specific gravity	.782	.740

The bromin absorption value of the fractions volatile at 100° C., were as follows:

	Distillate of liquid A (up to 100° C.)	Distillate of liquid B (Up to 100° C.)
Total bromin	123	145

thus showing that the product produced by compressing the gases and vapors, and cooling the same under pressure contains — larger proportion of unsaturated volatile bodies than did that produced by cooling and condensing the vapors, without compression.

[fol. 1522] Experiment 6: Crown Diamond oil was treated in a converter at a temperature of —° C., the gases and vapors entered and left the compressor as shown below:

Entering Compressor

Pressure	Temperature
Atmospheric	131-136° C.

Leaving Compressor

Pressure	Temperature
125 lbs. sq. in.	92-99° C.

showing a drop in temperature of about 38° C., (37 to 39° C.).

Experiment 7: With a Mexican solar oil split at about the same temperature the following results were obtained:

Entering Compressor	
Pressure	Temperature
Just below normal	190-200° C.
Leaving Compressor	
Pressure	Temperature
120 lbs. sq. in.	110-120° C.

showing a drop in temperature of about 80° C.

The above figures on temperatures at the inlet and outlet of the compressor give some idea of the fall in temperature obtained and illustrate the greater fall of temperature obtained when working at higher admission temperatures. From Experiment 2 it will be seen that even when we deal with liquids condensing about 100-150° C. not only does the vapor from the condenser contain far more of these liquids, but the liquids have different physical and chemical constants. The last mentioned test confirms the results of test described above.

In all cases, the yield of condensate boiling below 160° C. obtained from any given oil when passing the cracked products and vapors from the converter through the compressor is about one-third greater than the amount which is obtained when the products from the converter are directly condensed. This is, in itself, strong evidence that the compressor has caused a deep-seated reaction. The different physical and chemical constants possessed by the product obtained after passing through the compressor, conjointly with the drop in temperature taking place in the compressor, point most definitely to one explanation, and one only, namely, the formation of unsaturated hydrocarbons in the compressor cylinder, the production of which is accompanied by an absorption of heat. Not only does this interesting physicochemical action increase the yield of liquid fuel and diminish the gas produced, but the liquid fuel so formed consists for the most part of unsaturated hydrocarbons, which have a high heat value and these are, for the most part, very volatile liquids which are particularly desirable in a liquid fuel required for high speed internal combustion engines.

The use of mechanical compression on a mixture of the hot vapors and gases with the direct object of producing endothermic reactions is, I believe, entirely new. It is particularly valuable in that it is applicable to work in conjunction with any oil splitting process whatsoever. When it is taken into consideration that ordinary splitting processes generally yield a spirit which is inferior to the actual petrol (gasolene) as regards proportion of lower boiling point fractions and consequently inferior as a motor fuel, the great value of this discovery is made more obvious.

Experiment 8: The oil treated was American petrolite, a distillate having the following properties:

Specific gravity ..... 8150.
Flash-point ..... 94° F.

	Fraction per cent.	Total per cent. over
First drop 110° C.		
110° to 120° C.	1.0	1.0
120 " 130 "	0.5	1.5
130 " 140 "	1.0	2.5
140 " 150 "	5.0	7.5
150 " 160 "	5.0	12.5
160 " 170 "	3.5	16.0
170 " 180 "	3.5	21.5
180 " 190 "	6.5	28.0
190 " 200 "	7.0	35.0
200 " 210 "	5.5	40.5
210 " 220 "	6.0	46.5
220 " 230 "	5.5	52.0
230 " 240 "	7.5	59.0
240 " 250 "	7.0	66.0
250 " 260 "	8.0	74.0
260 " 270 "	7.5	82.0
270 " 280 "	5.0	87.0
280 " 290 "	5.5	92.5
290 " 300 "	4.0	96.5

Residue, 3.5 per cent.

Specific gravity of the fractions boiling at—

100°—200° C. 7775
200 —230 " 8097
230 —260 " 8375
260 —300 " 8424

In this test the petrolite was cracked at 600° to 700° C., under pressure of 75 pounds, as above, the gases and vapors were passed through the first separator to separate out carbon, tar, etc., and thence through the second separator at about 200° C., and the liquid collected in said second separator used in making a second run. The gases entered the compressor at about 100° C., where the pressure was raised, from about atmospheric up to 120 pounds per square inch. A drop in temperature of about 20 degrees C. was noticed.

The following products were produced, in the first run (from petrolite alone):

Motor fuel, sp. gr.	.760	51.3%
Residue (light)	.847	33.3%
Residue (heavy)	.857	3.9%
Gas and loss		11.5%
		100.00%

The light residue from above, sp. gr. 847, run without any fresh oil:

Motor fuel, sp. gr.	.769	37.64%
Light residue		45.09%
Heavy residue		7.84%
Gas and loss		9.43%
		100.00%

The total result of the two runs was:

Motor fuel	63.9%
Residue	21.5%
Gas and loss	14.6%
[fol. 1523]	100.00%

Experiment 9: The "light residue" produced as in experiment 8, was mixed with the petrolite, and the mixture run through the converter, with the production of the following:

Motor fuel, sp. gr.	.760	63.68%
Residue		20.28%
Tailings		.59%
Gas and loss		15.45%

In operating in this manner, the plant has been run continuously for 24 hours without choking taking place, and so far as I have been able to ascertain it might be run for an indefinite period if cleaned from heavy residue by blowing steam through the converter and separators for a quarter of an hour once in every twelve hours.

Gas oil or solar oil, specific gravity .850, can be dealt with satisfactorily in place of the petrolite, but if the price is higher, no advantage would be gained, as the yield of motor fuel is lower, as might be expected from the result of cracking the .847 residue alone.

I prefer to speak of the product as "fuel" rather than as "spirits," because in the minds of many people the latter term indicates products all distilling below about 120° C., and in this liquid there are considerable fractions distilling above this temperature, the use of which, in a motor-car engine, is rendered possible by the presence of constituents of lower boiling point than any present in ordinary petrol or gasolene, or by the larger percentages volatile at 120° C., these constituents imparting an ease in starting engine from cold and a flexibility in running which should render the new fuel a popular substitute for petrol.

The condensation together under pressure by the pressure hereinbefore described of the heavier hydrocarbon gases with the vapors of the lighter hydrocarbon liquids, gives a product from which the gases show but little tendency to escape at ordinary temperatures. When the liquid is drawn from the collecting tank the escape of the less easily liquified gases and expansion cause the liquid to be cooled down below the freezing point of water, and when this liquid is brought into a warm room it shows beads of escaping gas for a short time, but this soon ceases and the liquid shows no effervescence such as would occur had the gases been merely dissolved in a cool liquid hydrocarbon under pressure. On distilling the motor fuel it is found that from 9 to 11% of its constituents pass off as gases and vapors which are not re-condensed under ordinary conditions, and the presence of these gives the fuel a higher vapor pressure which is invaluable in the starting of the engine in cold weather.

I give the following comparison of the vapor pressure of the fuel with that of "Pratt's No. 1 Perfection petrol" with the following results:

Vapor Pressure in Inches of Mercury

Temperature	My fuel	Pratt's No. 1 petrol
12.8° C	2.15	0.7
15.5 "	3.8	1.4
18.3 "	5.8	2.6
21.1 "	7.8	3.6
23.9 "	9.8	4.8
26.7 "	12.0	5.9
29.4 "	14.2	7.1
32.3 "	16.3	8.25
35. "	18.4	9.3
37.8 "	20.6	10.5

So that the vapor pressure of my fuel may be taken as about double that of Pratt's.

The high pressure of the vapor suggests that trouble might arise through the overheating of a can of the fuel left on the top of a car in the hot sun but under these conditions even if the whole bulk of the liquid became heated to 100 degrees, the pressure on the sides of the can would only be 10 pounds to the square inch, as against 5 pounds given by ordinary petrol, and the cans would stand a much higher pressure than this.

The loss in volume and increase in specific gravity on exposure to air are not as high as might be expected from the vapor pressure. Comparative experiments with No. 1 Pratt's petrol gave the following results:

Evaporation from a Surface of 21 Sq. Inches at Ordinary Temperature

Time exposed	My fuel	Pratt's No. 1
1½ hours	14.6%	13.9%
3 "	18.2%	19.4%
4½ "	21.0%	25.2%

After this point was reached the evaporation of the petrol became far more rapid than that of my fuel.

The determination of the calor-fic value of a highly volatile liquid of this character is fraught with many difficulties and the use of a bomb calorimeter is unsatisfactory owing to the difficulty in preventing loss by escape of vapor during the weighing of the liquid and the violence of the explosion.

Vaporizing the spirit in any form of lamp or burner from a wick cannot be employed owing to the heavy fractions of high boiling point present and this difficulty was finally surmounted by atomizing the spirit by pressure in a small reservoir mounted on a balance and burning the volatized spray in a burner properly dimensioned to insure complete combustion in a Junker calorimeter.

Three determinations, in each of which — grams of the fuel were consumed were made, the temperature readings [fol. 1524] being closely concordant and the calorific value (per 10 grams) calculated from them being:

My Fuel

	Gross		Net	
1	10,462	calories.	9,841	calories.
2	10,560	"	9,940	"
3	10,493	"	9,873	"
Mean	10,505	"	9,884.7	"
	18,906.	B. T. U.	17,622	B. T. U.

Pratt's No. 1 Spirit

1	10,330	calories.	9,709	calories.
2	10,145	"	9,463	"
3	10,132	"	9,226	"
Mean	10,202.3	"	9,466	"
	18,366	B. T. U.	17,046.3	B. T. U.

While figures given for Pratt's spirit by several observers are higher than these determinations, the latter are strictly comparative and show the calorific value of my fuel to be slightly higher than that of No. 1 petrol, (about 3% higher in this test) a result borne out by bench tests made with the following comparative results:

Although the bench test was made on a cold morning, the engine started well with my fuel, and showed perfectly smooth running even with reduced load.

The measurements for the five sets of tests are summarized below:

	My fuel	Pratt's No. 1
1. Full load test:		
Revolutions per minute	1,000	1,000
Kilo-watts, load	2.93	2.99
Gallons per hour	0.69	0.85
Gallons per kilo-watt hour	0.236	0.284
2. Acceleration test:		
Revolutions per minute	1,300	1,300
Kilo-watts, load	2.36	2.37
Gallons per hour	0.76	1.12
Gallons per kilo-watt hour	0.322	0.473
3. Reduced load test:		
Revolutions per minute	1,000	1,000
Kilo-watts, load	Nil.	0.40
Gallons per hour	0.52	0.67
4. Test at normal speed:		
Revolutions per minute	1,000	1,000
Horse power	14.5	13
Gallons per hour	1.41	1.67
Gallons per horse power-hour	0.097	0.128
5. Test at increased speed:		
Revolutions per minute	1,300	1,300
Horse power	17	17
Gallons per hour	1.66	2.02
Gallons per horse power-hour	0.098	0.120

The exhaust from the engine when running with my fuel was very free from smoke and had no objectionable odor, while Pratt's No. 1, produced both smoke and odor.

It will be noticed that my fuel showed the greatest economy over petrol in the acceleration test and reduced load test, this being due to the rapidity with which the fuel --rms the explosive mixture and so insures --xibility in running.

Experiment 10: In order to more fully compare the products produced by treatment in the same manner, from "petrolite" and from the "light residue," the two liquids, were treated separately, producing products of the following properties:

	Motor spirit from "petrolite"	Motor spirit from second residue
Specific gravity	.760	.769
Flash point	Below 60°F.	Below 60°F.
First drop	25°C.	25°C.
Residue and gas	15%.	15.25%

Distilling between—	Fraction %	Total % over	Fraction %	Total % over
25° and 30° C.	.0	.0	1.00	1.00
30 " 40 "	1.75	1.75	1.25	1.25
40 " 50 "	2.5	4.25	2.75	5.00
50 " 60 "	2.75	7.0	2.75	7.75
60 " 70 "	3.0	10.0	3.0	10.75
70 " 80 "	3.0	13.0	3.25	14.0
80 " 90 "	2.5	15.5	2.75	16.75
90 " 100 "	4.0	19.5	3.25	20.0
100 " 110 "	5.0	24.5	4.0	24.0
110 " 120 "	3.5	28.0	3.5	27.5
120 " 130 "	3.0	31.0	3.0	30.5
130 " 140 "	6.25	37.25	4.5	35.0
140 " 150 "	6.25	43.5	5.0	40.0
150 " 160 "	7.0	50.5	4.75	44.75
160 " 170 "	7.5	58.0	6.0	50.75
170 " 180 "	3.0	61.0	7.25	58.0
180 " 190 "	5.25	66.25	5.5	63.5
190 " 200 "	5.25	71.5	5.0	68.5
200 " 210 "	3.25	74.75	2.5	71.0
210 " 220 "	4.25	79.0	6.5	77.5
220 " 230 "	2.0	81.0	3.25	80.75
230 " 240 "	2.0	83.0	2.5	83.25
240 " 245 "	2.0	85.0	1.5	84.75

	Specific gravity			
Fraction 25° to 80°	.6912	.7462	.8937	.7470
" 80 to 120	.7522		.7543	
" 120 to 150	.7740		.7865	
" 150 to 200	.7987		.8118	
" 200 to 230	.8320		.8419	

The residual gas from the process consists of those gaseous products of the decomposition which are non-liquefiable under the conditions of the experiment. It is composed largely of saturated and unsaturated hydrocarbons, and has a calorific value of 1442.6 British thermal units per cubic foot. The quantity yielded varies slightly with the quality of the oil and other factors, but is approximately 12 cubic ft. per gallon of oil cracked. The high thermal

value of the gas makes it a valuable fuel, and it could be used for heating the converters, but it might be found profitable to compress it in cylinders for use in autogenous soldering, or for other purposes.

Experiment 11: An attempt was made to analytically determine the nature and proportions of the permanent gases escaping condensation and also those liquefied, absorbed or combined with the condensing spirit.

Using an American "petrolite" oil with a specific gravity of .815 it was found that on the average 12 cubic feet of permanent gas was formed per gallon of oil subjected to the cracking and condensing process and left the apparatus [fol. 1525] as gas after the compression and condensing had taken place.

Samples of the escaping gas were analyzed and were found to have the following composition:

Ethylene	31.1
Ethane	25.4
Methane	34.6
Hydrogen	8.9
	100.0

and its calorific value as determined in the Junker's calorimetter was 1442.6 British thermal units per cubic foot.

The determination of calorific value affords a valuable check on the analysis, as, if the analysis be correct, calculations from it should give a calorific value closely approximating to the result obtained experimentally in the calorimeter.

Ethylene	31.1×1712=	53243.2—B. T. U.
Ethane	25.4×1912=	48564.8—B. T. U.
Methane	34.6×1073=	37157.9—B. T. U.
Hydrogen	8.9× 347=	3083.3—B. T. U.
		142427.2—B.T.U. per 100 cubic feet
		1424.2—B.T.U. per cubic foot

So that I have:

Calculated	1424.2 B. T. U. per cu. foot
Determined	1442.6 B. T. U. per cu. foot

a result well within the errors of calculation and so confirming the analysis.

A portion of the finished fuel from the run made in Experiment 11, after being drawn off and after being allowed to stand until signs of "beading" had ceased and the liquid had been allowed to be warmed up to the temperature of 16° C. was distilled up to 150° C., and the gases and vapors escaping conednsation by water cooling were collected and analyzed and were found to consist of:

Unsaturated hydrocarbons	73.4
Saturated hydrocarbons	26.5

The gas left after absorption by fuming sulphuric acid, on exploding with oxygen yielded carbon dioxide and water vapor in the ratio of 3 to 4 which points to its being propane or a mixture of butane, propane and ethane, while the whole gas on explosion with oxygen gave carbon dioxid and water vapor in the ratio by volume of 5 to 4.1 which strongly points to the unsaturated hydrocarbons consisting (in part) of higher members of the acetylene series a view confirmed by the original fuel giving a heavy precipitate with mercuric chlorid.

Experiment 12: A portion of the original fuel from the run made in Experiment 11, when subjected to ultimate analysis gives as figures:

Carbon	85.9
Hydrogen	12.76

a carbon-hydrogen ratio of 6.73 to 1, the carbon being in excess of that required by either the saturated or ethylene series and pointing to the motor fuel being a mixture of these with an even less saturated compound.

The bromin absorption given by the fraction of the fuel distilled up to 150° C. is 101.8 but after acid treatment and steam distillation the distillate gives a bromin absorption number of only 44.7 while the original motor fuel produced in some of the runs gave a bromin absorption number as high as 150; this pointing to the light fractions containing highly unsaturated hydrocarbons.

A point of great value is that the pressure of these highly volatile bodies formed during compression of the gases and vapors at temperatures above 100° C. gives the motor

fuel such excellent starting power even in the coldest weather, that it is possible to successfully use fractions of the oil distilling as high as from 200° C. to 230° C., or even 240° C.

In most of the experiments made so far, I have obtained products having greater heat-producing properties (higher B. T. U.) than ordinary .76 gasolene, combined with larger fractions volatile at a temperature below 80° C. or 100° C., than are present in ordinary .76 gasolene, and a much lower flash point than is possessed by ordinary .76 gasolene, and my products have greater efficiency per gallon than ordinary .76 gasolene, as shown by both road and bench tests.

The product appears to always contain considerable amounts of unsaturated hydrocarbons, and to possess the valuable properties of slow burning, quick igniting, and absence of knocking. The specific gravity of the product is, in most of the experiments made so far, above .75 and the highest gravity produced so far is about .80 or slightly higher. The flash points of these two were both lower than the gasolenes of the same gravity.

In another bench test of the power developed by an engine using the fuel, engine No. 1 had the following dimensions: Bore 121 m. m., stroke 140 m. m., this engine being the Tilling Stevens, well-known motor bus type. The petrol employed was "Taxibus" having a specific gravity of .759 at 10° C., my fuel .790 at 15.55° C. "Taxibus" having a high specific gravity is more efficient than the lighter qualities.

The following table gives the results of the tests at various speeds:

Consumption, pints per H. P.-hour

Horse power	M. P. M.	My fuel	Taxibus
51.41	1,175	.569	.636
42.9	900	.582	.645
36.3	775	.566	.661
29.7	620	.575	.649

[fol. 1526] The average consumption was:

My fuel ..... .573 pints per brake-horse-power-hour.
Taxibus ..... .647 " " " " " "

and by weight—

My fuel	.565	lbs. per brake-horse-power-hour.
Taxibus	.613	" " " " " "

These figures show a saving with my fuel of 11.4% by volume and 7.8% by weight, for the same brake-horse-power-hour.

Engine No. 2: Further tests were made with a high speed Vauxhall engine, 95 m. m. bore by 140 m. m. stroke. In this instance the petrol had a specific gravity of .730.

Runs were made with this engine at the following speeds and horse powers:

Revolutions per minute	Horse power
720	19.5
1,140	33
1,650	47
2,040	52
2,280	46

The average economy of my fuel over .73 petrol was 9.05% by volume.

In order to obtain the best results with my fuel, slight adjustment of the carbureters was required with both engines to give the best air and fuel proportions.

In addition to running the motors at the maximum speeds runs were made at very slow speeds and the engine given a sudden throttle valve opening. At the slow speed of 150 revolutions per minute the running was quite as steady as with petrol, and quick acceleration was obtained with the opening of the throttle valve; in fact my fuel gave results equal to, or better than, petrol under all conditions of load and throttle opening.

Road tests were made with a Siddeley Deasy car fitted with Knight motor 90 m. m. bore by 130 m. m. stroke. Before taking the final test runs the car was run for some hundreds of miles on my fuel in order to ascertain if there were any difficulties in use, such as carbonization, fouling of ignition plugs, imperfect acceleration, smoking at the exhaust and difficulty in carburetion under varying load conditions. With the carbureter adjusted for the fuel, the running was quite as good as with the petrol. The exhaust has a slightly more pungent odor than petrol, but at no time

has it been necessary to give any attention to the ignition plugs. The fuel does not appear to cause any detrimental deposit within the cylinders.

The carbureter employed was known as the "Ideal," which is fitted with a jet adjustable from the driving seat. It was therefore quite easy to run petrol and my fuel alternately, and to make comparative tests as to power on grades. However, as accurate results are difficult to obtain on the high roads the final running tests were made at a race track.

The total weight of the car and load was 3,572 lbs., and was run with its usual fittings, wind screen, etc. The petrol employed had a specific gravity of .730.

The following results were obtained:

At 20 miles per hour:

My fuel	25.6 miles per gallon.
Petrol	24.4 " " "

At 35 miles per hour:

My fuel	20.4 miles per gallon.
Petrol	19.6 " " "

The average consumption was:

My fuel 23 miles per gallon=36.6 ton miles per gallon.
Petrol 22 miles per gallon=35.08 ton miles per gallon.

The car was run on both fuels at the highest possible speed with the following results:

My fuel, 50 and 51 miles per hour.
Petrol, 49 and 52 miles per hour.

The test hill, grade one in four, was taken with both fuels at a minimum speed of 12 miles per hour from a standing start.

The results of these tests enable me to state that my fuel is the best substitute for petrol that has been, so far, brought to my notice. It is without any doubt more economical than petrol. In every test made on the bench and on the road the consumption has in every case been less than petrol for the same work.

As further illustrating the high specific gravity and low boiling points of the product of my process, as distinguished

from ordinary gasolene, I will state that in all instances the gravity is higher than that of a gasolene of the same boiling point range.

As above stated my fuel contains a considerable amount of aromatic hydrocarbons, which amount will vary depending upon the various factors, such as kind of oil treated, temperature of converter, temperature of the cut, amount of pressure produced in the compressor and other factors. In many instances I have been able to make this fuel combine with its own weight, or even more than its own weight of nitric acid, forming nitro-aromatic compounds, in this respect differing from ordinary gasolene, which does not unite with nitric acid.

The odor of the refined fuel is quite different from that of petrol or gasolene. If ordinary gasolene or petrol, which is practically all composed of saturated hydrocarbons, such as "Pratt's Perfection spirit" or "Standard Shell spirit" be mixed with denatured ethyl alcohol, in about equal volumes, then approximately two-thirds of the gasolene will be found to be miscible and one third will remain undissolved immiscible. Substantially the same result is obtained when my new fuel is so treated but if the fuel treated with sulphuric acid, and the saturated portions after being washed and refined, be mixed with alcohol, the saturated [fol. 1527] portion will not be at all miscible, either in ethyl or methyl alcohol.

When the fuel is treated with a small amount of acid, such as sulfuric acid, a sweet aromatic odor is produced, entirely different from the odor of gasolene. The fuel always contains a certain amount of aromatic hydrocarbons such as benzol and toluol, and also contains considerable amounts of unsaturated hydrocarbons, of the olefin and acetylene series, the amounts of such unsaturated portion varying between 20% and 50%. The iodin and bromin numbers of the fuel are in accordance therewith.

As above stated, this fuel has a higher caliorific value than gasolene and will give about 15% more miles per gallon, in the average motor car.

In using my new fuel, in an automobile engine, there is no difficulty in starting in cold weather, its acceleration is good, and it does not appear to give rise to the formation of carbon deposit within the cylinders to a degree detrimental to the running of the engine.

While in some of the above examples, I have described certain definite temperatures and pressures used in the decomposing retorts, certain definite temperatures and pressures used in the step of removing the solid carbon, tarry matters, certain temperatures and pressures at the inlet and outlet of the compressor, and the like, I call attention that these are for purposes of illustration only, and not as limiting the invention, since I claim herein, the product, irrespective of how the same is prepared.

The boiling point, flash point, distillation table, percentage of unsaturated compounds, percentage of benzol, toluol, etc., amount of acetylene compounds, etc. will depend upon a large number of particular factors, such as the particular oil used, the temperature and pressure in each step of the process, rate at which the oil is fed into the decomposer, and possibly other factors.

The process herein described may be carried out in an apparatus such as is shown in the accompanying drawing, which apparatus forms the subject matter of my co-pending application 77,357 filed Feb. 9, 1916. In said drawing oil is forced by the pump 1, through the superheating coil 2, heating coil 4, located in a space 3, heated by burners 5. 6 is a pyrometer placed between the coils of the pipe 4. The gases and vapors pass by pipe 7 past the pressure regulating valve 8, into a first cooler 9, surrounded by a cooling jacket 10, and filled if desired with a suitable filling material 11, and any heavy condensate collected therein being drawn off through pipe 12. The gases and uncondensed vapors flow by pipe 13 to a second similar cooler 14, in which a light condensate may separate out, which may be drawn off through pipe 15, to be again introduced from pump 1 into the heating coils. The gases and vapors leaving the upper part of the tower 14, for example at a temperature of 160 to 200° C., pass through a trap 16, wherein a portion of the mist carried by the gases may separate out, and be returned to the tower 14 by means of the pipe 16*. The gases and vapors are then compressed in the pump 17, wherein the endothermic reaction takes place, and are passed by pipe 18 to condensers 19 and 20, the condensate collecting in tank 21, and the uncondensed gas escapes through the pipe 22.

While I have described this product suitable for use as a motor fuel, it can obviously be used for other purposes,

for example by nitration, products useful in the manufacture of explosions, dyes, and the like may be produced.

This application is in part a division and continuation of my copending applications as follows:

Serial Number 824,194—filed March 12, 1914,
Serial Number 829,634—filed April 6, 1914, and
Serial Number 3,955—filed January 23, 1915.

in which applications I have claimed the processes described herein. The refined motor fuel described herein is not specifically claimed herein, but in my copending application 26,395, filed May 6, 1915.

What I claim is:

1. A liquid fuel for use in automobile engines having larger fractions boiling at temperatures below 80° C. than any hydrocarbon distillate of the paraffin series with a similar specific gravity and having an initial boiling point at least as low as that of ordinary gasolene, and a calorific value and specific gravity both higher than that of ordinary gasolene, said fuel being relatively free from liability to pre-ignite.

2. A liquid fuel for use in automobile engines having larger fractions boiling at temperatures below 80° C. than a paraffin hydrocarbon distillate with a similar specific gravity and having an initial boiling point at least as low as ordinary gasolene, and a specific gravity at least as high as ordinary gasolene, said fuel being relatively free from liability to pre-ignite, slow burning but igniting quickly, the fuel before refining being of a yellow color, and when evaporated leaving a dark orange non-drying substance with a strong varnish-like odor, the odor disappearing with the coloration by distilling said fuel with mineral matter of the fullers' earth type, said fuel being distinguishable from a product produced by simply a solution of a gas in a liquid, [fol. 1528] by no greater loss in fractionation than results from the fractionation of ordinary gasolene.

3. A crude motor fuel produced from mineral oil said fuel having a yellow coloration and peculiar odor and depositing resinous sticky matter on evaporation the coloring matter and odor being substantially all removable by filtration through fullers' earth said fuel having a gravity not

below about .76 and a calorific value greater than ordinary gasolene.

4. A motor fuel characterized by the properties of slow burning rapid ignition, flash point and initial boiling point at least as low as those of ordinary gasolene, and having relatively large fractions volatile at low temperature, said fuel having a greater calorific value than ordinary gasolene.

5. A motor fuel containing unsaturated hydrocarbons, said fuel commencing to boil materially below 35° C., not less than about 23% of said spirit being volatile at temperatures below 100° C., said spirit having a specific gravity of not less than .76.

6. A liquid fuel for use in automobile engines having larger fractions boiling at temperatures below 100° C., than any straight gasolene with a similar specific gravity, and having initial boiling point and flash point at least as low as those of ordinary gasolene.

7. A motor fuel suitable for use in internal combustion engines, having gravity between .75 and .81, and having a carbon to hydrogen ratio of about 6.73 to 1.

8. A motor fuel having a gravity of about .76, and having larger fractions volatile below 80° C., than ordinary gasolene of the same gravity, and containing considerable amounts of hydrocarbons having less hydrogen than would correspond to the formula C_nH_{2n+2}.

9. A motor fuel of a gravity of between .75 and .80, said fuel containing not less than about 19% volatile at a temperature of 100° C.

10. A hydrocarbon product having a gravity between .75 and .80, containing olefin hydrocarbons, acetylene hydrocarbons, and aromatic hydrocarbons, said product having a carbon to hydrogen ratio of about 6.73 to 1, and having large fractions volatile at 80 and 100° C.

11. A hydrocarbon product having aprpoximately the following distillation table:

Temperature	Fraction %	Total over %
Between 25 and 50° C.	4.25 to 5.00	4.25 to 5.00
" 50 " 80	8.75 to 9	13 to 14
" 80 " 100	6.5 to 6	19.5 to 20
" 100 " 130	11.5 to 10.5	31 to 30.5
" 130 " 160	18.5 to 14.25	50.5 to 44.75
" 160 " 200	21 to 23.75	71.5 to 68.5
" 200 " 230	9.5 to 12.25	81 to 80.75
" 230 " 245	About 4	85 to 84.75

12. A hydrocarbon product of a gravity about .76 to .77, of which the vapor pressure at 26.7° C. is equal to about 12 inches of mercury.

13. A hydrocarbon product of a gravity of about .76 to .77, of which the vapor pressure, at all temperatures between 12.8 and 37.8° C. is materially higher than that of ordinary gasolene of the same gravity, said product having a carbon to hydrogen ratio greater than a product consisting solely of olefins.

14. A motor fuel having a boiling point range of at least from 33° C. to 140° C., and having a gravity between .76 and .77, said product having a carbon to hydrogen ratio greater than a product consisting solely of olefins.

15. A motor fuel containing ethylene hydrocarbons, acetylene hydrocarbons and aromatic hydrocarbons, having a carbon to hydrogen ratio of about 6.73 to 1, and having a fraction not materially below 19.5% volatile at 100° C.

16. A motor fuel of a gravity of .75 to .80 containing endothermic hydrocarbons, and having a carbon to hydrogen ratio materially greater than that of a product consisting solely of olefin hydrocarbons.

17. A motor fuel, having a gravity of about .76, of which not less than 40% distils at temperatures not over 150° C., said fraction having a bromin number not below 100, the carbon to hydrogen ratio of the fuel being about 6.73 to 1.

18. A motor fuel having a gravity between .75 and .81 having a larger fraction volatile at 100° C., than ordinary gasolene, having a bromin absorption number not below 135, a carbon to hydrogen ratio of about 6.73 to 1, containing olefin hydrocarbons, acetylene hydrocarbons and aro-

matic hydrocarbons, having a higher vapor pressure than ordinary gasolene, having not less than 23% volatile at 100° C., said fraction having a sulfuric acid absorption number of about 76 and a bromin absorption number not below about 150.

19. A motor fuel having a gravity of not below .755, not less than 23% of which distils at temperatures below 100° C., said fraction having a sulfuric acid absorption number of about 76, said fuel in the unrefined state having a yellow color, which color is removable by distillation with fullers' earth.

20. A motor fuel having a gravity of between .75 and .80, the fraction distilling below 100° C. having a sulfuric acid absorption number not below 76.

21. A motor fuel having a gravity of between .75 and .80 the fraction distilling below 100° C. having a bromin number not below 150, said fuel in the unrefined state having a yellow color, which color is removable by distillation with fullers' earth.

[fol. 1529] 22. A motor fuel having a gravity of between .75 and .80, the fraction distilling below 100° C. having an iodin number not below about 256, said fuel in the unrefined state having a yellow color, which color is removable by distillation with fullers' earth.

23. A motor fuel having a gravity of between .75 and .80 said fuel containing olefin hydrocarbons, acetylene hydrocarbons and aromatic hydrocarbons, and said fuel having a vapor pressure at 26.7° C., equal to about 12 inches of mercury.

24. A hydrocarbon product having a gravity of not less than .74, commencing to distil below 50° C., the fraction distilling below 100° C. having a bromin number not less than 145, said fuel in the unrefined state having a yellow color, which color is removable by distillation with fullers' earth.

25. A motor fuel of a gravity not less than .755 of which not materially less than 23% is volatile at 100° C.

26. A motor fuel of a gravity not less than .755, the fraction thereof distilling below 100° C. having a bromin number of about 150, the entire fuel having a carbon to hydrogen ratio greater than that of a product consisting solely of ethylene hydrocarbons.

27. A liquid fuel having approximately the composition when analyzed of carbon 85.9, hydrogen 12.76, a carbon-hydrogen ratio of about 6.73:1, the carbon being in excess of that required by either the saturated or ethylene series.

28. A liquid fuel yielding when distilled up to 150° C., gases and vapors uncondensed by water cooling, containing about 73.4% of unsaturated hydrocarbons, the gas left after absorption by fuming sulfuric acid on exploding with oxygen yielding carbon dioxid and water vapor in the ratio of about 3:4 and the whole gas on explosion with oxygen giving carbon dioxid and water vapor in the ratio of 5:4.1.

29. A motor fuel consisting essentially of hydrocarbon materials, and containing aromatic hydrocarbons, open-chain saturated hydrocarbons, olefin hydrocarbons, and acetylene hydrocarbons, said fuel having a carbon to hydrogen ratio not far from 6.73 to 1, having a gravity above .76, and having a lower flash point than a saturated distillate of the paraffin series of the same gravity, and a higher calorific value than such a distillate.

30. A hydrocarbon liquid having a calorific value about 3% greater than that of a gasolene of the same gravity.

In testimony whereof I have affixed my signature hereto.

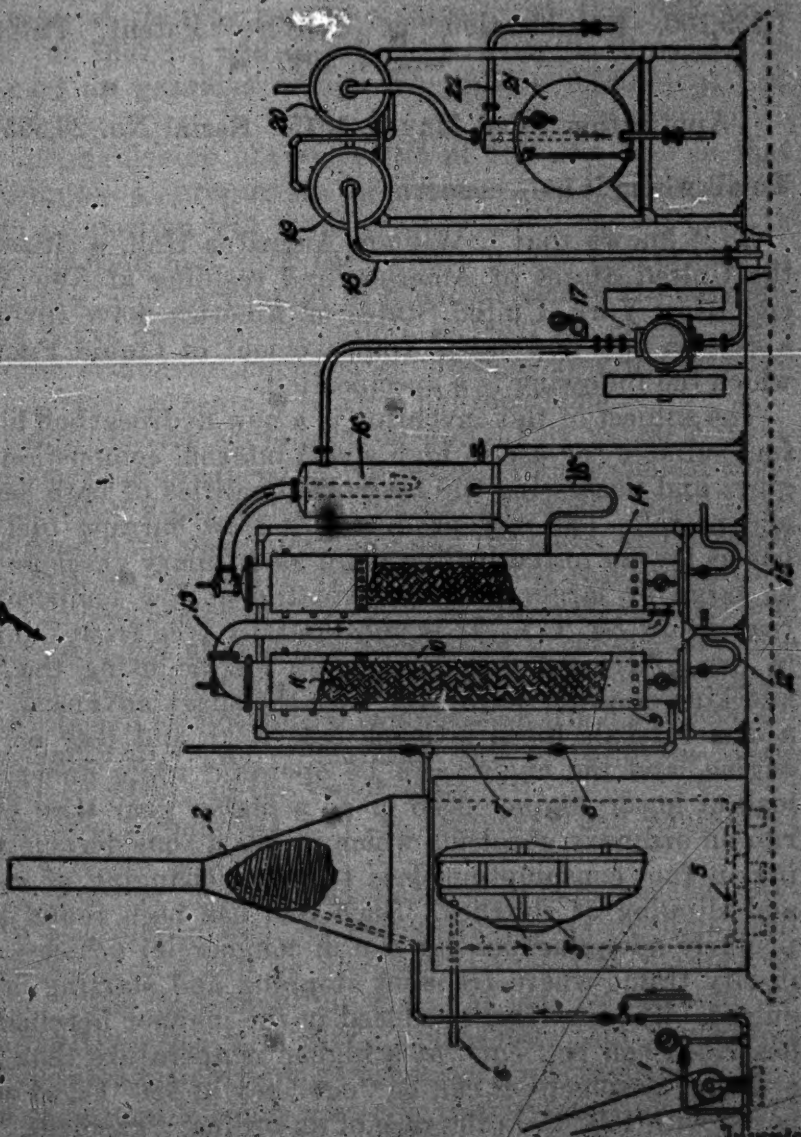
William Augustus Hall.

Witnesses: Ripley Wilson, O. J. Worth.

[fol. 1530] EXHIBIT No. 512

W. A. HALL.
LIQUID FUEL.
APPLICATION FILED MAY 6, 1915.

1,239,100. Patented Sept. 4, 1917.



Witnesses
H. Pennock

Inventor
Wm A. Hall
by A B Foster
Attorney

[fol. 1531] United States Patent Office

William A. Hall, of New York, N. Y.

Liquid Fuel

1,239,100. Specification of Letters Patent. Patented Sept. 4, 1917

Application Filed May 6, 1915. Serial No. 26,395

To all whom it may concern:

Be it known that I, William Augustus Hall, a citizen of the United States of America, and residing at New York city, New York, United States of America, have invented a certain new and useful Improvement in Liquid Fuel, of which the following is a specification.

The subject of this invention is a new hydrocarbon liquid fuel suitable for use in high speed internal combustion engines and possessing the desirable qualities of both benzol and petrol. The new product is a slow burning fuel yet has as low an initial boiling point as ordinary gasolene and as large or larger fractions volatile at low temperature (say below 80° C.). It is substantially free from liability to pre-ignite and therefore in an engine using the fuel knocking does not occur even with the spark advanced. As a direct result there is much less wear and tear on the engine, and the engine can be operated while under full load at lower engine speed or on a higher gear than when run on ordinary gasolene, which means a considerable saving in fuel consumption, less frequent changing of gears and slipping of clutches. Such fuel has been found particularly advantageous for use in commercial vehicles and in city traffic where frequent stopping and starting is required. The new fuel produced in the manner hereinafter described can be "cut" at a higher temperature than can ordinary gasolene—it can be "cut" say at 180° C., as compared with 160° C. in the case of an ordinary gasolene. Its larger fractions volatile at low temperature have been found to carry complete combustion to the fractions volatile only at the highest temperatures, a considerably increased mileage per gallon consumed being the result.

The low flash point and low initial boiling point give in an engine run on the fuel great ease in starting in cold weather, and owing to its large fractions volatile at low temperatures great flexibility and quickness of acceleration is obtained. It has been found that as great flexibility and ease of starting can be obtained with this fuel when "cut" at 180° C., and of specific gravity 0.760 as can be obtained on gasolene of specific gravity 0.730 "cut" at 160° C.

A distinguishing characteristic of the new fuel is that it contains a proportion of unsaturated hydrocarbons which proportion will naturally vary with the oil used in its production and with the details of the operation. It contains a large percentage of hydrocarbons of the ethylene series but is nevertheless quite free from the objectionable features ordinarily inherent in products containing more than a small percentage of such hydrocarbons.

The fuel having these peculiar and highly valuable properties may be produced by an endothermic chemical reaction between a gas which would be permanent under ordinary conditions of temperature and pressure, and a vapor of a hydrocarbon spirit, which vapor, if condensed to a liquid in the customary manner at atmospheric temperature, would not answer the purpose of a satisfactory motor fuel, the combination of the permanent gas and vapor being effected by mechanical compression while at a temperature sufficiently high to maintain said hydrocarbon spirit largely or wholly in the vapor state.

The new liquid fuel may be compared and contrasted with petrol as follows:

The new fuel possesses an abnormally high specific gravity in accordance with its boiling points as distinguished from petrol and can be nitrated in the same manner as benzol. The fact that this material can be nitrated, by treating the same with nitric acid, shows that it contains considerable proportions of aromatic hydrocarbons.

In one example it has a specific gravity of about .767, yet on fractionation has an initial boiling point of about 33° C., all boiling below 150° C., 60% boiling below 100° C.; a straight gasolene distillate having such fractionation would have a specific gravity of about .70.

The new fuel readily nitrates, due to the presence of aromatic hydrocarbons combining with its own weight or more of nitric acid and in this respect, differing from petrol which does not nitrate.

The odor of the new fuel when fully refined is quite different from that of petrol or gasolene.

The new fuel is also characterized by having a much greater vapor tension.

When a very little acid is added to the new fuel, a sweet aromatic odor is produced.

The new fuel contains a certain amount of the aromatic series of hydrocarbons, (benzol and toluol); it always contains a certain amount of unsaturated hydrocarbons (or hydrocarbons of the ethylene series, and some hydrocarbons more unsaturated than the ethylenes) varying be-
[fol. 1532] tween 20 and 50% and its iodin and bromin numbers are in accordance therewith.

The new fuel may be distinguished from gasolene by the following mode of identification:—If a natural gasolene distillate that is practically all saturated, such as Pratt's perfection spirit and standard shell spirit, be mixed with denatured ethyl alcohol half and half, then approximately ⅔ of this mixture will be found that is miscible and ⅓ will remain uncombined, non-miscible. Substantially the same result is obtained when the new fuel is so treated, but if the unsaturated portions of the new fuel be separated and taken off by sulfuric acid absorption and the saturated portions, after being washed and refined, be mixed with alcohol, the saturated portion will not be at all miscible either in ethyl alcohol or methyl alcohol.

This spirit has a higher calorific value than gasolene and will give about 15% more miles per gallon in the average motor car.

Another characteristic is that it will evaporate more rapidly than gasolene or even than benzol.

The fuel has a combustion of approximately 85.9% of carbon and 12.76% of hydrogen, corresponding to a carbon to hydrogen ratio of 6.73 to 1, the carbon being in excess of that required by either the saturated or ethylene series of hydrocarbons due to the presence of aromatic and acetylene hydrocarbons. The liquid yields, when distilled up to 150° C., more or less of gases and vapors uncon-

densed by ordinary water cooling, these gases containing about 26.6% of unsaturated hydrocarbons. When this gas is treated with fuming sulfuric acid, then mixed with oxygen and exploded, carbon dioxid and water vapor in the ratio of 3 to 4 (by weight) are produced, and the gas without the sulfuric acid treatment, when being mixed with oxygen and exploded giving carbon dioxid and water vapor in the ratio of 5 to 4.1.

The following table indicates in detail the fractions of the new fuel boiling at temperatures differing by 10° C.

Sp.G. ..... 767 I. B. P.	33° C.
Boiling up to 50° C.	2 %
" " " 60	10 %
" " " 70	22 %
" " " 80	35 %
" " " 90	55 %
" " " 100	61 %
" " " 110	71.5%
" " " 120	82 %
" " " 130	89 %
" " " 140	95 %
" " " 150	All over.

I call attention particularly to the very large amounts of material volatile at temperatures between 80 and 100° C., as shown in the above table.

The new fuel may be produced from paraffin mineral oil by a process consisting of the following steps:

(1) Cracking an oil—(which may be crude, "gas," fuel, lamp or almost any distillate that in itself has a range of boiling temperature that would not permit its use as a fuel in the ordinary automobile engine)—in a continuous tube of small size (1 to 3 inches in diameter) and of sufficient length, at an average temperature, of from 540° C. to 600° C. on the exterior of the tube and under pressure preferably of about 75 lbs. per square inch, with a speed of flow of oil in the pipe regulated to produce a maximum of cracking with a minimum of fixed or permanent gas consistent with economy of operation.

(2) Expanding the product subsequent to the cracking operation by reducing the pressure.

(3) Cooling the vapors and gases when in this expanded state and from them separating such portions as condense below the point at which the "cut" is to be made—usually from 180° C. to 200° C.

(4) Producing an endothermic chemical reaction between the gas and vapors by compressing in a mechanical compressor to a pressure preferably from 100 to 125 lbs. per square inch all the gas that has been produced along with all the vapors that boil below the temperature of the "cut," admitting these into the cylinder of the compressor at a temperature sufficiently high that they enter while in the state of vapor and mist, the fixed gas that has not been attached being permitted to separate after cooling under pressure, subsequent to the mechanical compression and be collected for other use.

(5) Clarifying and deodorizing the product by extracting the yellow resinous colloidal matter which it contains, preferably by distilling it in the presence of a small amount of fuller's earth.

The process herein described may be carried out in an apparatus such as is shown in the accompanying drawing. In said drawing oil is forced by the pump 1, through the superheating coil 2, heating coil 4, located in a space 3, heated by burners 5. 6 is a pyrometer placed between the coils of the pipe 4. The gases and vapors pass by pipe 7 past the pressure regulating valve 8, into a first cooler 9, surrounded by a cooling jacket 10, and filled if desired with a suitable filling material 11, and any heavy condensate collected therein being drawn off through pipe 12. The gases and uncondensed vapors flow by pipe 13 to a second [fol. 1533] similar cooler 14, in which a light condensate may separate out, which may be drawn off through pipe 15, to be again introduced from pump 1 into the heating coils. The gases and vapors leaving the upper part of the tower 14, for example at a temperature of 180 to 200° C., pass through a trap 16, wherein a portion of the mist carried by the gases may separate out, and be returned to the tower 14 by means of the pipe 16a. The gases and vapors are then compressed in the pump 17, wherein the endothermic reaction takes place, and are passed by pipe 18 to condensers 19 and 20, the condensate collecting in tank 21, and the uncondensed gas escapes through the pipe 22.

In my copending application 26,546, I have described and claimed a crude motor fuel, produced in accordance with the process described herein, certain of the claims of said application being broad enough to cover also the refined fuel.

This application is in part a continuation of my copending applications as follows:

Serial No. 824,194—filed March 12, 1914,
Serial No. 829,634—filed April 6, 1914,
Serial No. 3,955—filed January 23, 1915,

in which applications I have claimed the process described in the present application.

I do not herein claim the process and apparatus herein described, the same being claimed in the cases above enumerated, and in my Patent 1,175,909 and in my copending application 77,375 filed February 9, 1916.

I claim:

1. A water-white liquid fuel having the composition when analyzed of approximately carbon 85.9%, hydrogen 12.76%, having a carbon to hydrogen ratio of about 6.73 to 1, said fuel having a specific gravity of not materially below .76, a materially larger percentage of the same being volatile at 100° C., than would be the case with ordinary gasoline, said fuel containing ethylene hydrocarbons and aromatic hydrocarbons, said fuel being further characterized by the properties of slow burning, rapid ignition, having flash point and initial boiling point at least as low as those of ordinary gasoline and high bromin absorption value, said fuel being substantially free from yellowish resinous, colloidal matter.

2. A refined liquid fuel having approximately the compostion when analyzed of carbon 85.9, hydrogen 12.76, a carbon hydrogen ratio of 6.73 to 1, the carbon being in excess of that required by either the saturated or ethylene series, said fuel being substantially free from yellowish resinous, colloidal matter.

3. A motor fuel which when treated with sulfuric acid in amount sufficient to remove the unsaturated portions, leaves a saturated liquid substantially all of which is immiscible with either methyl alcohol or ethyl alcohol, said

fuel containing aromatic hydrocarbons, open-chain saturated hydrocarbons, and open-chain unsaturated hydrocarbons.

4. A liquid fuel having about 35% volatile at 80° C., and a specific gravity of not less than .76, having an initial boiling point at least as low as that of ordinary gasolene, said fuel being substantially free from resinous matter, said fuel containing aromatic hydrocarbons, open-chain saturated hydrocarbons, and open-chain unsaturated hydrocarbons.

5. A liquid fuel having a gravity not below .76, about 35% thereof being volatile at 80° C., said fuel being free from yellowish, colloidal, resinous matter, said fuel containing aromatic hydrocarbons, open-chain saturated hydrocarbons, and open-chain unsaturated hydrocarbons.

6. A refined motor fuel characterized by the properties of slow burning, and rapid ignition, said fuel having flash point and initial boiling point at least as low as those of ordinary gasolene, having fractions volatile at 80° C., and at 100° C., at least as large as those of ordinary gasolene, said fuel being substantially free from yellowish, resinous, colloidal matter, said fuel containing aromatic hydrocarbons, open-chain saturated hydrocarbons, and open-chain unsaturated hydrocarbons.

7. A water-white motor fuel containing considerable quantities of unsaturated hydrocarbons, said fuel having an initial boiling point below 35° C., having a specific gravity of not less than .76, and having materially larger fractions volatile at 100° C., than would be the case with ordinary gasolene, said fuel being substantially free from yellow, resinous, colloidal matter, and having a carbon to hydrogen ratio of about 6.73:1.

8. A water-white motor fuel suitable for use in internal combustion engines having a specific gravity not materially below .76, and having a carbon to hydrogen ratio of 6.73 to 1, said fuel being substantially free from yellowish, resinous, colloidal matter.

9. A water-white motor fuel having a gravity of about .76, having as much as 35% volatile at 80° C., all of said fuel distilling below 150° C., said fuel being substantially

free from yellowish, resinous, colloidal matter, said fuel containing aromatic hydrocarbons, open-chain saturated hydrocarbons, and open-chain unsaturated hydrocarbons.

10. A water-white hydrocarbon product having a gravity [fol. 1534] not materially below .76, containing olefin hydrocarbons and open-chain hydrocarbons more unsaturated than the olefins, (said fuel being substantially free from yellowish, resinous, colloidal matter, and not materially less than 35% of said fuel being volatile at 80° C.

11. A liquid hydrocarbon motor fuel, having a gravity of not less than .76, and containing aromatic hydrocarbon, olefin hydrocarbons and hydrocarbons more unsaturated than olefin hydrocarbons, not less than about 35% of said fuel being volatile at 80° C., and not less than about 61% of said fuel being volatile at 100° C., said fuel having a carbon to hydrogen ratio of about 6.73 to 1, and having a higher calorific value than ordinary gasolene, said fuel being substantially free from yellowish, resinous, colloidal matter.

12. A substantially water-white motor fuel consisting essentially of hydrocarbons, and containing aromatic hydrocarbons, olefin hydrocarbons and hydrocarbons more unsaturated than the olefins, said fuel having a gravity of not less than about .76, said fuel being substantially free from yellowish, colloidal, resinous matter, and having a carbon to hydrogen ratio of substantially 6.73:1.

13. A motor fuel, having a boiling point range of at least from 33° C. to 140° C., being substantially water white free from col-oidal, resinous, yellowish matter in solution, and having a carbon to hydrogen ratio of about 6.73 to 1.

14. A water-white motor fuel containing ethylene hydrocarbons, aromatic hydrocarbons, and open-chain hydrocarbons more unsaturated than olefin hydrocarbons, not less than about 60% of said fuel being volatile at 100° C., said fuel being substantially free from yellowish, colloidal, resinous matter.

15. A motor fuel of a gravity of over .76 of which not less than about 61% is volatile at 100° C., said fuel being substantially free from yellowish, colloidal, resinous matter.

16. A motor fuel having substantially the following fractionation table:

Boiling	up	to	50° C	2 %
"	"	"	60° C	10 %
"	"	"	70° C	22 %
"	"	"	80° C	35 %
"	"	"	90° C	55 %
"	"	"	100° C	61 %
"	"	"	110° C	71.5%
"	"	"	120° C	82 %
"	"	"	130° C	89 %
"	"	"	140° C	95 %
"	"	"	150° C,	Substantially all

said product being free from resinous coloring matter, substantially as described.

17. A water-white motor fuel having a gravity of .76, of which about 35% is volatile at 80° C., and about 61% is volatile at 100° C., said fuel being substantially free from yellowish, resinous, colloidal matter.

18. A motor fuel having a gravity of .76, containing between about 20% and about 50% of unsaturated hydrocarbons and having not less than about 35% volatile at about 80° C.

19. A motor fuel having substantially the 75 following fractionation table:

Boiling	up	to	50° C	2 %
"	"	"	60° C	10 %
"	"	"	70° C	22 %
"	"	"	80° C	35 %
"	"	"	90° C	55 %
"	"	"	100° C	61 %
"	"	"	110° C	71.5%
"	"	"	120° C	82 %
"	"	"	130° C	89 %
"	"	"	140° C	95 %
"	"	"	150° C,	substantially all.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

William A. Hall.

Witnesses: H. D. Jameson, Harold E. C. Fairweather.

[fol. 1535] EXHIBIT No. 513

L. DE FLOREZ.

PROCESS OF MAKING MOTOR FUEL.

APPLICATION FILED DEC. 4, 1917. RENEWED JUNE 29, 1922.

1,437,045. Patented Nov. 28, 1922.

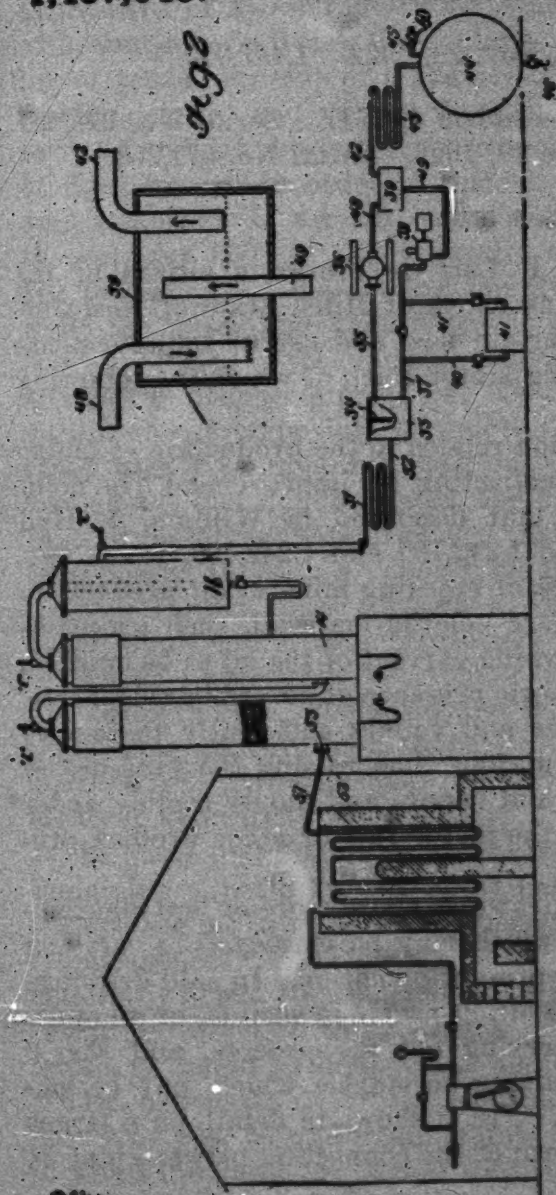


Fig 2

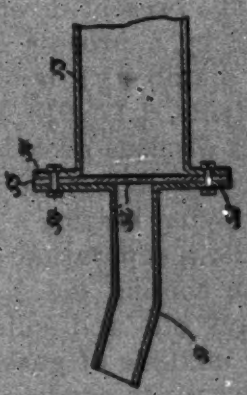


Fig 3

Fig 1.

Witnesses

Inventor.

Luis de Florez

A. B. Fatten

[fol. 1536] United States Patent Office

Luis de Florez, of Short Hills, New Jersey, Assignor to Motor Petrol Company, of New York, N. Y., a Corporation

Process of Making Motor Fuel

Patented Nov. 28, 1922. 1,437,045

Application Filed December 4, 1917. Serial No. 205,290. Renewed June 29, 1922. Serial No. 571,768

To all whom it may concern:

Be it known that I, Luis de Florez, a citizen of the United States, residing at Short Hills, State of New Jersey, have invented certain new and useful Improvements in Processes of Making Motor Fuel, of which the following is a specification.

The present invention relates to the production of motor fuel by a process constituting an improvement (in point of simplicity) upon that described in William A. Hall Patents, 1,175,910 and 1,242,795 and 1,242,796, which patents disclose processes of cracking mineral oil products to produce lighter or more volatile material, such processes involving heating a flowing current of the oil to be cracked, under a superatmospheric pressure of several atmospheres, then cooling the gases and vapors sufficiently to remove heavy oils and solid matter, then raising the pressure of the mixture of gases and vapors and finally cooling under pressure to condense the motor fuel or other product produced.

The accompanying drawings show, more or less diagrammatically, apparatus which may be employed in carrying out the process of my present invention. In said drawings Fig. 1 shows a side elevation partly in section, of an apparatus suitable for carrying out the process, and Fig. 2 shows one form of mixing receptacle which may be employed at 39 (Fig. 1). Fig. 3 shows in detail, on a larger scale, the preferred form of the connection between pipe 51 and pipe 53.

In producing the motor fuel in accordance with my present invention, I pass a gas oil or a similar hydrocarbon oil

or distillate, for example that known as "American petrolite," or crude oil, or crude kerosene, or other hydrocarbon oil less volatile than gasoline, through a coil of pipes, heated to a temperature of about 500 or 600° C., in which the material undergoing treatment is maintained under a pressure of about four to six atmospheres (a pressure of 5 atmospheres being particularly suitable in the cracking of crude kerosene of a gravity of .8). I then pass the resulting gases and vapors through dephelgmating apparatus of any suitable construction which may take the form of filled towers, in order to remove the major portion of such materials as are not volatile at the temperature of the cut, say 200° C. (or generally at temperatures from 140 to 220° C.), this cooling operation being performed while the gases and vapors are at a pressure materially below that used in the cracking coils and may be performed at about atmospheric pressure. To this end, the pipe connecting the decomposing coil and the first condenser is provided with a suitable constriction. (See Fig. 3.) After leaving the last dephlegmator, for example that shown at 14 in the accompanying drawings (and after the gases have been passed through a vapor trap 16 if desired). I pass the vapors and gases through a condenser 31, cooled to about atmospheric temperature, say 25 to 30° C., in order to condense practically everything which is non-volatile at this temperature. The gases and liquids then constituting the flowing mixture both contain considerable amounts of unsaturated hydrocarbons, notably olefines and more highly unsaturated hydrocarbons.

The gases and liquids pass through pipe 32 to a trap 33 containing a baffle 34, the gases passing by pipe 35 to a compressor 36, in which they are compressed to about 5 to 7 atmospheres. I preferably do not employ a pressure of materially above 10 atmospheres in this operation, since it is not my intention to produce a liquefaction of such materials as would be liquefied at higher pressures.

The condensate separated from the gases in the trap 33 passes by pipe 37 and pump 38 into a mixing receptacle 39 in which the gases are mixed with the liquid, and partially absorbed thereby. It is sometimes desirable to by-pass the liquid from pipe 37 through a pipe 40, to any suitable refining or treating devices, represented diagrammatically at

41 (which may include chemical purification, absorption of impurities by fuller's earth or the like, fractional distillation or other suitable operations for the removal of any impurities which may be present) after which the liquid passes by pipe 41' back to the pipe 37 and thence to the pump 38, by which the liquid is pumped into the mixer 39, wherein it is mixed with the gases from the compressor 36. The gases may also be purified between 34 and 39 if desired. It is not necessary to employ any catalyst in the mixer 39. The gases and liquids together then pass by pipe 42 into a cooler 43 and into a collecting tank 44 and [fol. 1537] any unabsorbed gases pass out through pipe 45 past the pressure-reducing valve 60, set at any desired pressure, e. g., 5 to 7 atmospheres, and can be used for heating the retort if desired. The liquid is drawn off by pipe 46, and constitutes the motor fuel. Suitable thermometers are provided at T, for measuring or recording the temperatures.

Fig. 2 shows one form of mixing receptacle 39 which may be employed in carrying out the process. In this form of apparatus the gas under pressure enters by pipe 48 from the compressor 36, and the liquid material condensed in the coil 31 and separated in the trap 33 (either with or without passing through the purifier represented diagrammatically at 41) enters by pipe 49. The mixture of gas and liquid leaves by pipe 42 to the cooling or refrigerating coil 43 (see Fig. 1).

Fig. 3 shows the connection preferably employed between the coil of pipe forming the cracking coil and the pipe leading to the condenser. In said figure 51 illustrates the end of the small pipe of which the cracking coil is constructed, which may be a one-inch pipe. The end of this pipe is provided with a flange 52. 53 is a large pipe, leading to the first condenser, and this is provided with a flange 54. Between these two flanges is placed the plate 55 which is provided with a small hole 56. Assuming for illustration that the cracking coil and pipe 51 are one-inch (internal diameter) steel pipe, and that oil is being fed into the converter at a rate of three gallons per minute, and that the temperature of the gases and vapors in 51 is about 605° C., and that the pipe 53 is about six inches in internal diameter. To maintain a pressure of about 70 lbs. per square inch

in the coil, the plate 55 may be provided with a hole of (say) one-half inch size. A number of plates with different sized holes may be provided, whereby removing the bolts 58 and substituting a plate with a larger or smaller hole, other conditions may be maintained in the cracking coil. This example is given merely by way of example, and without limiting myself to the details thereof.

I desire to state that I do not claim anything shown or described in the W. A. Hall patents above referred to.

The present case contains matter disclosed in my prior application 90,388 filed April 11, 1916.

It is sometimes advantageous to line or partly fill the pipe 53 with a suitable catalyst, e. g., one containing over 50% of carbon and less than 50% of iron, as described and claimed in my copending application 90,387 filed April 11, 1916. This feature is optional in the process constituting the present invention.

What I claim is:

1. A process of making motor fuel which comprises (*a*) cracking under a superatmospheric pressure of several atmospheres and at an elevated temperature, a flowing current of hydrocarbon material containing fractions not sufficiently volatile to serve as constituents of motor fuel, (*b*) removing from the gases and vapors substantially the entire amount of those fractions having boiling points above about 200° C., while at a pressure below that used in the cracking operation, and while leaving in the vapor state, substantially the entire amount of material volatile at such temperature, (*c*) cooling the remaining mixture of gases and vapors to about atmospheric temperature, to condense the major portion of the vapors as a light liquid, (*d*) compressing the remaining gases to a pressure not over about ten atmospheres, (*e*) and absorbing the same in said light liquid while under approximately that pressure.

2. A process of making motor fuel which comprises (*a*) cracking a hydrocarbon oil containing fractions having boiling points above those of ordinary gasolene, while under a pressure of about four to six atmospheres, (*b*) removing from the gases and vapors the major portion of those fractions having boiling points above 200° C., while

at a pressure materially below that used in the cracking operation, (*c*) cooling the remaining mixture of gases and vapors to about atmospheric temperature while at such reduced pressure, to condense the major portion of the vapors, and thereby produce a light liquid, (*d*) purifying said light liquid, (*e*) compressing the remaining gases to a pressure of not over about ten atmospheres, and (*f*) absorbing the same in said light liquid, while under superatmospheric pressure.

3. In the production of motor fuel the step of bringing together a cracked hydrocarbon liquid containing no considerable quantities of fractions of which the boiling points are above about 200° C., and a cracked hydrocarbon gas, such liquid and such gas both containing substantial amounts of unsaturated hydrocarbons, at not below atmospheric temperature, and at a superatmospheric pressure of about 5 to 7 atmospheres, in the absence of a catalyst, and thereafter cooling the mixture.

4. In the production of motor fuel the step of bringing together a refined cracked hydrocarbon liquid containing no considerable quantities of fractions of which the boiling points are above about 200° C., and a cracked hydrocarbon gas, such liquid and such gas both containing substantial amounts of unsaturated hydrocarbons, at not below atmospheric temperature, and at a superatmospheric pressure [fol. 1538] of about 5 to 7 atmospheres, in the absence of a catalyst, and thereafter cooling the mixture.

5. In the production of motor fuel, the steps of (*a*) cracking a mineral oil containing fractions having boiling points above the boiling point range of ordinary gasoline, by subjecting the same to a cracking temperature while under a pressure of several atmospheres, (*b*) cooling the resulting gases and vapors to not below about 200° C. and separating the condensate, (*c*) cooling the remaining gases and vapors to normal atmospheric temperature, (*d*) treating the condensate of step *c* with the uncondensed gases while under a pressure of about four to six atmospheres, while out of contact with the condensate of step *b*.

6. In the production of motor fuel, the step of mingling under a pressure of not over ten atmospheres, and at ap-

proximately normal atmospheric temperature, a cracked hydrocarbon liquid, substantially all of which is volatile at 200° C., and which contains considerable amounts of unsaturated hydrocarbons, and hydrocarbon gases containing considerable amounts of unsaturated hydrocarbons, in the absence of a catalyst.

In testimony whereof I affix my signature.

Luis de Florez.

[fol. 1539] EXHIBIT No. 601

Nov. 4, 1926. Walter N. Carpenter, Shorthand Reporter

Department of Commerce, Bureau of Standards

S. W. Stratton, Director

Circular of the Bureau of Standards No. 98

[August 24, 1920]

Recommended Specifications for Volatile Mineral Spirits for Thinning Paints

Prepared and Recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, July 26, 1920; P. H. Walker, Bureau of Standards, Chairman; J. W. Ginder, Treasury Department, Secretary.

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, The Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specifications to a large number of representatives of the petroleum industries and the paint and varnish industries, and gave careful consideration to the replies which were received in time.]

[fol. 1540] Contents

	Side page
1. General	1540
2. Detection and removal of separated water	1541
3. Sampling	1541
4. Laboratory examination	
5. Basis of purchase	

1. General

These specifications apply only to petroleum distillates, known as mineral spirits.

The oils delivered under these specifications shall be genuine and shall conform to the following requirements:

Appearance.—Shall be clear and free from suspended matter and water;

Color.—Shall be "water white";

Spot Test.—Shall evaporate completely from filter paper;

Flash Point.—Shall be not lower than 30° C (86° F) when tested in a closed cup tester;

Sulphur.—Shall be absent, as determined by the white-lead test;

Distillate below 130° C (266° F) shall not exceed 5 per cent;

Distillate below 230° C (446° F) shall be not less than 97 per cent;

Reaction.—Shall be neutral.

[fol. 1541] 2. Detection and Removal of Separated Water.

Draw a portion by means of a glass or metal container with a removable stopper or top, or with a "thief," from the lowest part of the container, or by opening the bottom valve of the perfectly level tank car. If water is found to be present, draw it all out, record the quantity, and deduct it from the total volume of liquid delivered.

3. Sampling

The method of sampling given under (*a*) should be used whenever feasible. When method (*a*) is not applicable, method (*b*), (*c*), or (*d*) is to be used, according to the special conditions that obtain.

(*a*) While Loading Tank Car or while Filling Containers for Shipment.—Samples shall be drawn by the purchaser's inspector at the discharge pipe where it enters the receiving vessel or vessels. The composite sample shall be not less than 5 gallons and shall consist of small portions of not more than 1 quart each taken at regular intervals during the entire period of loading or filling.

The composite sample thus obtained shall be thoroughly mixed, and from it three samples of not less than 1 quart each shall be placed in clean, dry glass bottles or tin cans, which must be nearly filled with the sample and securely stoppered with new clean corks or well-fitting covers or caps. These shall be sealed and distinctly labeled by the inspector; one shall be delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(*b*) From Loaded Tank Car or Other Large Vessel.—The composite sample taken shall be not less than 5 gallons and shall consist of numerous small samples of not more than 1 quart each taken from the top, bottom, and intermediate points by means of a metal or glass container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the stopper or top is removed and the

5062

[fol. 1542] EXHIBIT No. 602

Die

Prüfung und Verwendung des Erdöls, des Erdgases und der Erdölprodukte

Redigiert

von

C. Engler

Dr. phil. und Dr.-Ing. h. c.; Wirkl. Geh. Rat und Professor der Chemie an der Technischen Hochschule Friedericiana zu Karlsruhe

Unter Mitwirkung von

Dr. E. Czakó, Dr. G. Meyerheim, k. Baurat F. Nallinger, Dr. K. Pfeiffer, Dipl.-Ing. A. Freiherr v. Schmidt, Dr. E. Terres und Prof. Dr. L. Ubbelohde

bearbeitet von

Dr. D. Holde
Professor in Berlin

Dr. C. Koettnitz
Berlin-Lichterfelde

Dr. Leopold Singer
Fabrikdirektor in Düsseldorf

St. Goulischambaroff und **Dr. S. Aisinman**
Wirkl. Staatsrat in St. Petersburg — Fabrikdirektor in Bukarest

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Mit 368 Abbildungen

Leipzig
Verlag von S. Hirzel
1916.

jeden Grad je zwei Bestimmungen ausgeführt, aus welchen das Mittel gebildet wird. Sonst werden zwischen 20 und 50° wenigstens fünf, zwischen 20 und 150° wenigstens sechs Bestimmungen bei geeigneten Punkten ausgeführt, deren Ergebnisse zu einer Kurve vereinigt werden; aus letzterer können die Ausflußzeiten für die gewünschten Wärmegrade entnommen werden. Die Übereinstimmung der nach vorstehenden Bestimmungen ausgeführten Versuche ist eine gute. Bei den unterhalb 50° ausgeführten Versuchen betragen die Abweichungen der Einzelversuche vom Mittel für leichtflüssige und schwerflüssige Öle ±0,5 Proz., bei +50° betragen diese Abweichungen für leichtflüssige Öle bis zu ±0,5 Proz., für schwere Maschinenöle bis zu 1,6 Proz., für Zylinderöle bis zu 3,5 Proz. Auf verschiedenen Engler-Apparaten gibt das gleiche Öl bei +50° Abweichungen in der Zähflüssigkeit von höchstens 2,5 Proz. Öle, die bei normaler Wärme der Lager benutzt werden (Spindelöle, Maschinenöle), prüft man in der Regel bei 20 und 50°, selten bei 30 und 40°, Zylinderöle bei 50 und 100°, selten bei 150 und 180° (betrifft hauptsächlich Heißdampföle).

b) Änderungen der Zähflüssigkeit von Ölen. Einzelne dunkle Öle, welche feine feste Paraffin- oder Pechteilchen suspendiert enthalten, zeigen bei Zimmerwärme (20°) infolge von starken Temperaturschwankungen vor dem Versuch bis zu 15 Proz. des Flüssigkeitsgrades betragende Schwankungen. Durch vorangehendes Erhitzen finden Erniedrigungen der Zähigkeit bei 20° und durch starkes Abkühlen Erhöhungen der letzteren statt. Bei hellen und dunklen Destillatölen, welche in dünner Schicht keine festen Paraffin- oder Asphaltteilchen enthalten, treten die fraglichen Schwankungen nicht auf. Diese dürften meistens in der durch Erhitzen erfolgten Schmelzung und bei kurzem Abkühlen auf Zimmerwärme nicht völlig wiederkehrenden Abscheidung der festen Teilchen, bzw. in zu langsamer Schmelzung der durch starkes Abkühlen in vermehrter Menge ausgeschiedenen Paraffin- und Pechteile ihre Ursache haben. Bei künstlich mit Paraffin im Überschuß versetzten hellen Ölen wurde letztere Annahme durch Versuche bestätigt.

Die geschilderten Schwankungen sind bei Erzielung vergleichbarer Zähigkeitswerte gebührend zu berücksichtigen, indem man bei denjenigen Ölen, welche in dünner Schicht feine feste Teilchen erkennen lassen, von vornherein die Möglichkeit einer Veränderung der bei 20° bestimmten Zähigkeit um ±7 bis 8 Proz. zugibt oder neben der in üblicher Weise ausgeführten Bestimmung noch je eine mit dem 10 Min. auf 100° erhitzten und dem vorher auf −15° abgekühlten Öl vornimmt. Nur in besonderen Fällen, z. B. wenn die gefundenen Werte nahe einer vorgeschriebenen Grenze liegen, wird man den zweiten Weg wählen. Jedoch ist dabei zu bedenken, daß solche Öle, die bei Zimmerwärme feste Paraffin- oder Asphaltteilchen zeigen (Zylinderöle), in der Regel nicht bei 20° geprüft werden; bei 50° aber, wenn alle festen Teilchen geschmolzen sind, können die Schwankungen des Flüssigkeitsgrades naturgemäß nicht auftreten.

c) Abkürzung der Versuche und sonstige Abweichungen von der gewöhnlichen Versuchsausführung bei den Zähigkeitsbestimmungen. 1. Vierfacher Apparat. Zur gleichzeitigen Prüfung von vier Ölen dient das vierfache Viskosimeter (Anordnung von A. Martens), bei welchem vier Englersche Ausflußgefäße in einem großen Wasserbade W vereinigt sind (Fig. 46). Die Temperatur des Bades läßt sich hier durch das von der Turbine RS getriebene Schaufelrad T, Zufließenlassen von kaltem Wasser bei E oder Erwärmung des Bades durch eine kleine Gasflamme bequem regeln.

Für Versuche bei 100° benutzt man als Badflüssigkeit eine 20proz. wässerige Glyzerinlösung.

2. Abkürzung der Versuche durch Bestimmung der Ausflußzeit kleinerer Flüssigkeitsvolumina bei normaler Auffüllung.

Einem Hauptübelstand der gewöhnlichen Versuchsausführung beim Engler-Apparat, der zeitraubenden Dauer des Ausfließens von 200 cm³ Öl, kann man nach einem Vorschlag Holdes (bestätigt von Singer[1]), Edeleanu u. a.) dadurch begegnen, daß man die Ausflußzeit kleinerer Flüssigkeitsvolumina bestimmt und aus diesen die vorgeschriebene Ausflußzeit von 200 cm³ berechnet. Es stehen nämlich die Ausflußzeiten kleiner Volumina, z. B. 50 oder 100 cm³, der Öle zu der Ausflußzeit von 200 cm³ in einer für alle Öle gleichen proportionalen Beziehung, vorausgesetzt, daß die Öle nicht

1) Petroleum 2, 555. 1907.

5064

[fol. 1544]

Untersuchung der Mineralöle und Fette

sowie der ihnen verwandten Stoffe.

Von

Professor Dr. **D. Holde,**

Abteilungsvorsteher am Kgl. Materialprüfungsamt zu Gr.-Lichterfelde W.,
Dozent a. d. Technischen Hochschule Berlin.

Dritte, verbesserte und vermehrte Auflage.

Mit 92 Figuren.

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1909.

[fol. 1545]

Öle, die bei normalen Lagerschalenwärmen benutzt werden, also Spindelöl, Maschinenöle usw., werden in der Regel bei 20 und 50°, bei eingehender Prüfung auch noch bei 30 und 40°. Naßdampfzylinderöle bei 100° geprüft.

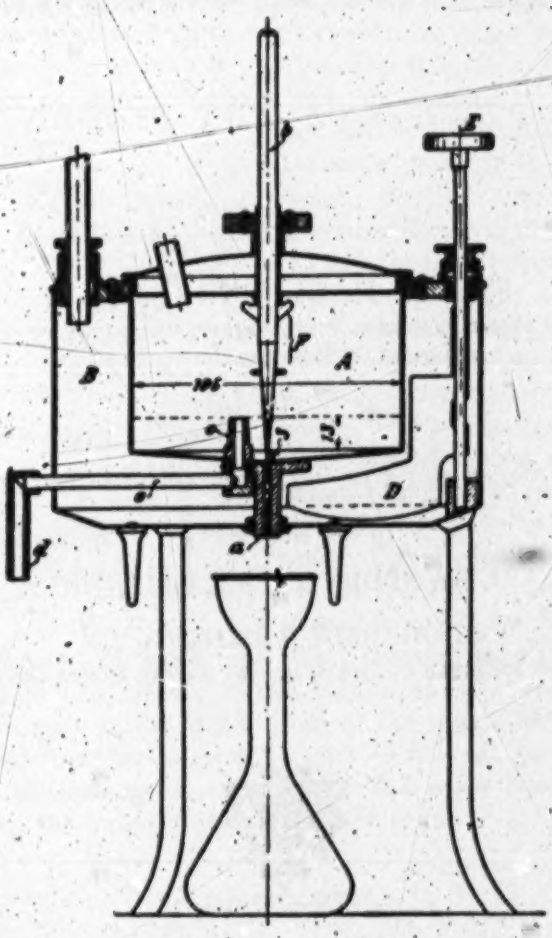

Fig. 39.

d) Zähigkeitsbestimmung bei sehr hohen Wärmegraden.

Da Zylinderöle in Heißdampfmaschinen Erwärmung bis zu 300° ausgesetzt sind, scheint ein Bedürfnis vorzuliegen, ihre Zähig-

5066

[fol. 1546]

EXHIBIT No. 604
Dec. 13, 1926.

OUTLINES

OF

INDUSTRIAL CHEMISTRY

A TEXT-BOOK FOR STUDENTS

BY

FRANK HALL THORP, PH.D.

ASSISTANT PROFESSOR OF INDUSTRIAL CHEMISTRY IN THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SECOND EDITION, REVISED AND ENLARGED

AND INCLUDING

A CHAPTER ON METALLURGY

BY CHARLES D. DEMOND, S.B.

TESTING ENGINEER OF THE ANACONDA COPPER MINING COMPANY

New York

THE MACMILLAN COMPANY

LONDON: MACMILLAN & CO., LTD.

1909

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its upper side. These pipes are closed at one end; the other opens into a distributing box (E). The liquor to be evaporated enters through (G), passes into (D), and flowing from the slots in thin films, is showered uniformly over the hot tubes (A), from whose outer surface the evaporation takes place. The liquor drips from tube to tube, collecting in the float box (F), from which the suction pipe of the centrifugal pump (H) draws it, to again pass over the tubes. The float in the box (F) operates a valve which allows fresh liquor to enter the effect just fast enough to replace that vaporized and what passes from the discharge pipe (J) as concentrated liquor. On (J) is a regulating valve governing the level of the liquor in (F) and thus controlling the rate of feed; the slower the discharge, the greater the concentration. The float completely closes the feed valve when the liquor rises to a definite height in (F); the discharge valve in the last effect thus automatically controls the flow of the liquor from effect to effect, by influencing the action of the feed valves. The tubes (A) are heated by live or exhaust steam, or by vapor from the preceding effect, which enters the steam chamber (B); the hot water condensed in (A) collects in the bottom of (B), and passing the steam trap, goes to the steam space of the next effect; thus being under great vacuum, it gives up part of its heat as steam, which assists in the heating of this effect. The vapor from each effect also enters the steam space (B) of the next.

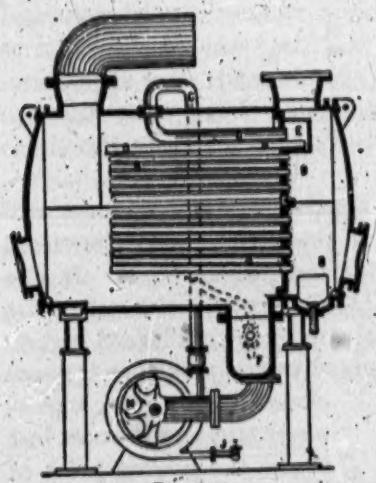

FIG. 4 a.

DISTILLATION

Distillation is the process of vaporizing a liquid and recovering it by condensing the vapors. The liquid formed by this condensation is called the distillate. Distillation is chiefly employed to separate a liquid from non-volatile matter dissolved or suspended in it; or to separate one liquid from a mixture of liquids of different boiling points; that one having the lowest boiling point being the first to begin to pass off as vapor.

But the separation of two liquids which are miscible with each

other is never complete by this means, and is less perfect the nearer their boiling points are together. Liquids which are miscible in all proportions, may be tolerably well separated, provided there are a few degrees difference in their boiling points, by employing the principle of *fractional condensation* of the vapors. This consists in passing the mixed vapors through a condenser which is kept at a constant temperature between the boiling points of the liquids. Thus the vapors of the high-boiling liquid being cooled below the boiling point of that liquid are condensed, while the vapors of the low-boiling liquid being still hotter than its boiling point, cannot condense, but pass on to another part of the apparatus, where they are condensed separately. When the high-boiling distillate condenses, it carries with it more or less of the low-boiling liquid, and hence should usually be returned to the boiler and redistilled. In such mixtures as this, there is a gradual rise in the boiling point during the entire distillation.

The chief parts of every distilling apparatus are the boiler or still and the condenser. In practical work the appliance for fractional condensation is placed between the still and the condenser. It may be an apparatus, called a "dephlegmator," in which the vapors are forced to bubble through a layer or column of the condensed higher-boiling liquid, as in a tower; or the mixed vapors may pass through chambers or a pipe, kept at a constant temperature, just above the boiling point of the low-boiling liquid. The still is usually iron, copper, or other metal, heated directly by a furnace, a steam jacket, or a coil.

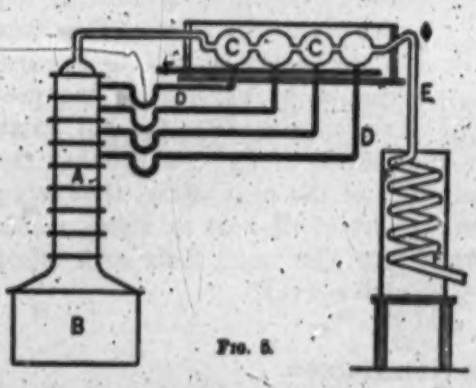

FIG. 5.

In Coupier's still (Fig. 5) a tower (A) is placed on top of the boiler (B); between the tower and the condenser is a series of bulbs (C, C) surrounded by a water bath, which may be kept at any desired temperature. While the mixed vapors are passing through the bulbs, the high-boiling constituents are condensed, and only the vapor of the more volatile liquid passes through (E) to the condenser (F). From each bulb a pipe (D) leads back to the tower, into which the condensed heavy liquid is delivered, to be redistilled or dephlegmated.

[fol. 1549]

The French column (Fig. 6) is very similar to the Coupier's apparatus, but instead of bulbs, a series of U-tubes (C) surrounded by a water bath is used. The column or dephlegmator (B) is divided into chambers by plates, each of which has a central opening covered by a dome; a small overflow pipe passes from each plate to the next. The vapors from the boiler (A) pass up through the central openings and bubble out under the edges of the domes through the layer of liquid on each plate. The liquid thus condensed flows down through the overflow pipes, and returns to the boiler.

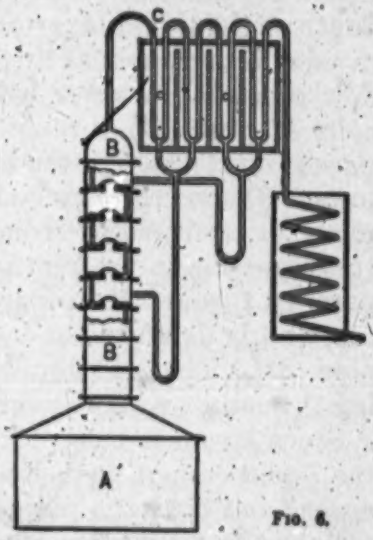

FIG. 6.

The Coffey still (Fig. 7) is much used for alcohol and gas liquor distillation. This consists of two towers, one, called the "analyzer" (E), receiving free steam from the boiler, and the other, called the "rectifier" (G), containing a long coil of pipe (C, C), through which

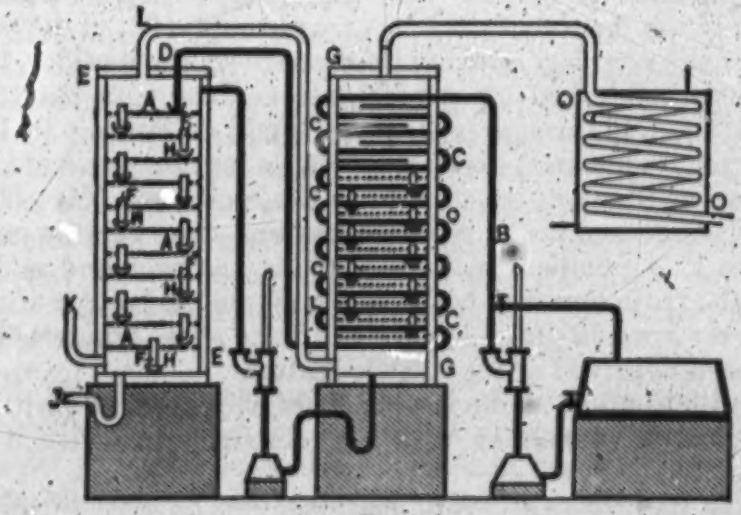

FIG. 7.

the liquid to be distilled flows on its way to the analyzer. The analyzer is divided into a series of chambers by horizontal, per-

[fol. 1550] forated plates (A); from each plate an overflow pipe (F) passes down and dips into a shallow cup (H) on the next plate below and holding liquid enough to form a hydraulic seat at the lower end of each overflow pipe. These pipes project about an inch, or an inch and a half above the plate in which they are set, thus determining the depth of the liquid layer on each plate. The rectifier is also divided into chambers by perforated plates, but it has overflow pipes in its lower half only. In the chambers lie the coils of pipe (C) through which the liquid to be distilled passes on its way to the analyzer. This still works as follows: Steam from the boiler is blown through (K) into the analyzer, and passes from the top of the analyzer through the pipe (L) to the rectifier. The liquid to be distilled is pumped through the pipe (B) and the coil (C) in the rectifier, and is delivered at the top of the analyzer through the pipe (D). The cold liquid is heated by the steam surrounding the coils, and is delivered hot at the top of the analyzer.

Since steam is being forced up through the perforations, the liquid cannot pass down through them, but is forced to spread out over the plate, and run down the overflow pipe (F) to the next plate, and so through the analyzer. The steam bubbling up through the thin layers of liquid, heats it very hot, and causes the volatile substances to distill off with the steam. This mixture of steam and volatile matter passes from the top of the analyzer, through (L), to the bottom of the rectifier. During its passage up the rectifier, the steam is condensed by coming into contact with the cold pipes (C, C), through which the liquid is flowing to the analyzer. Thus only the more volatile matters pass out at the top of the rectifier, and go to the condenser (O). The water condensed in the rectifier contains some volatile matter, so it is pumped to the top of the analyzer and mixes with the fresh liquor to be distilled. From the bottom of the analyzer a waste pipe (J) carries off the spent liquor which has been deprived of its volatile matter.

Distillation in vacuum is sometimes employed, and will be described in connection with the industries in which it is used.

Sublimation

Sublimation is the process of vaporizing a solid substance and condensing the vapors to again form the solid directly,

without passing through an intermediate liquid state. There are very few substances which vaporize without melting, but in all cases of sublimation, the change from the vapor to the solid state, is direct, and

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[fol. 1551] EXHIBIT No. 605

Dec. 14, 1926

In the United States Patent Office

To the Commissioner of Patents, Washington, D. C.

SIR: Your petitioner, Standard Development Company, a corporation organized and existing under the laws of the State of Delaware, and having a place of business at 26 Broadway, New York, New York, represents that in the matter of a certain improvement, for which Letters Patent 1,410,797 was granted March 28, 1922, on the application of Edgar M. Clark, your petitioner is the owner, by mesne assignment of the entire right, title and interest in said Letters Patent, as evidenced by assignment from said Edgar M. Clark to Standard Oil Company, a corporation of New Jersey, having a place of business in New York, New York, recorded September 9, 1921, liber G 114, page 95, and by assignment from said Standard Oil Company to your petitioner, Standard Development Company, dated 6th day of December, 1922 and recorded 4th day of May, 1923, liber F 119, page 66; and that petitioner has reason to believe that through inadvertence, or mistake, the specification and claims of said Letters Patent are too broad, including that of which said patentee was not the first inventor. Your petitioner, therefore, hereby enters this disclaimer to that part of the claim in said specification which is in the following words, to-wit:

"1. The improvement in the art of pressure distillation of petroleum oils for the purpose of producing lighter products by pyrogenesis, which consists in maintaining a considerable body of said oil under cracking conditions of temperature and pressure, continuously withdrawing oil from the said body, releasing the pressure from the withdrawn oil while the latter is in a heated condition, whereby its

lighter fractions will distill off, collecting such lighter fractions and returning them to the oil body for further cracking therein."

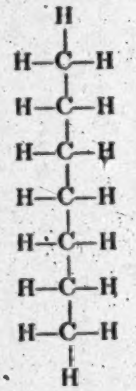
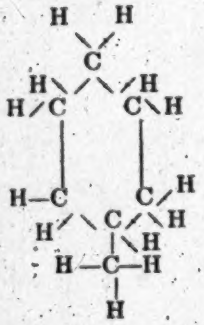
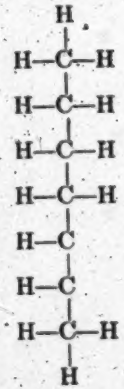
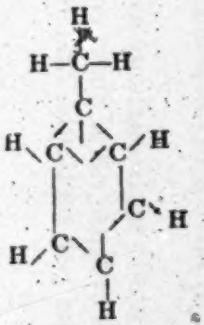
Executed by said Standard Development Company, through its duly qualified officers, at New York City, in the [fol. 1552] County of New York, and State of New York; this 11th day of November, 1925.

Standard Development Company, by C. A. Straw, Vice-President. Attest: H. M. McLarin, Secretary. Witnesses: —— ——.

EXHIBIT No. 606

Dec. 14, 1926

The probable structural formula of the four most common types of hydrocarbons, each being illustrated for the member of the series which contains seven carbon atoms, is as follows:

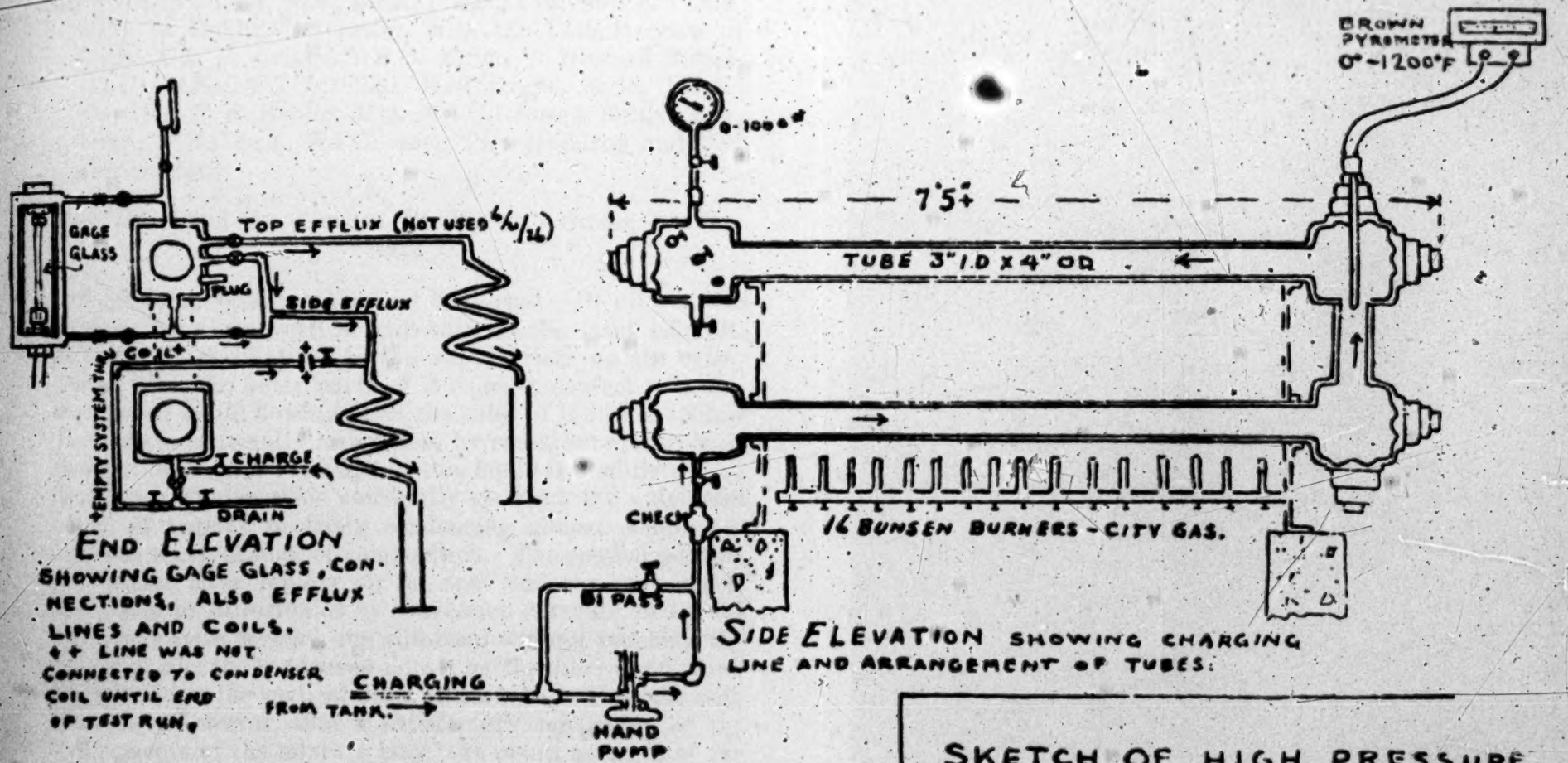
1. Broad Class 2. Narrow Class	Saturated Paraffin	Saturated Napthene	Unsaturated Olefin	Aromatic Aromatic
3. Probable Structural formula				
4. Chemical formula	(C_7H_{16})	(C_7H_{14})	(C_7H_{14})	(C_7H_8)
5. Individual name	Heptane	Methyl-cyclo hexane	Heptene	Toluene
6. Notes	(chain may also be branched)	(ring may contain from 4 to 8 carbon atoms)	(Chain may also be branched. May have more than two hydrogens missing)	(single rings always contain 6 carbon atoms. They may share two carbon atoms with another ring)

[fol. 1554] Some of the more complex types of hydrocarbons in petroleum may belong to two of these classes—for example, a compound might have a naphthenic ring and an olefinic side chain.

The asphaltic (unsaturated) hydrocarbons are not represented in the above series because all of them contain many more than 7 carbon atoms per molecule, and their precise structure is unknown.

(Here follows Defendants' Exhibit No. 610, side folio 1555.)

[fol. 1555]



END ELEVATION SHOWING GAGE GLASS, CONNECTIONS, ALSO EFFLUX LINES AND COILS.
++ LINE WAS NOT CONNECTED TO CONDENSER COIL UNTIL END OF TEST RUN.

SIDE ELEVATION SHOWING CHARGING LINE AND ARRANGEMENT OF TUBES.

SKETCH OF HIGH PRESSURE APPARATUS FOR CRACKING TEST.
SHOWING GAGE GLASS ATTACHMENT

[fol. 1556] EXHIBIT No. 611

Dec. 15, 1926

Distillation Principles and Processes

By Sydney Young, M.A., D.Sc., F.R.S., Professor of Chemistry in Dublin University, with the Collaboration of Lieut. Col. E. Briggs, D.S.O., B.Sc.; T. Howard Butler, Ph.D., M.Sc., F.I.C.; Thos. H. Durrans, M.Sc., F.I.C.; The Hon. F. R. Henley, M.A., F.I.C.; Joseph Reilly, M.A., D.Sc., F.R.C.Sc.I., F.I.C., with Two Hundred and Ten Illustrations

MacMillan and Co., Limited, St. Martin's Street, London.
1922

Inefficiency of Plain Vertical Still-head.—Of all possible forms, the plain vertical still-head is the least efficient. During the distillation, as the vapour rises up the cylindrical tube, the outer parts of it come in contact with the condensed liquid flowing down the sides of the tube. Since the tube is constantly losing heat by radiation and by conduction to the surrounding air, this liquid is slightly cooled and fresh condensation constantly goes on, the outermost layer of vapour probably condensing almost completely without much change of composition. The central portion of vapour rises rapidly up the tube and can only reach the liquid by diffusion or by convection currents, and much of it may pass through the still-head without reaching the liquid at all; the condensed liquid, on the other hand, flows rapidly down the vertical walls of the tube, back to the still. In order, however, that a satisfactory separation of the components of the mixture may take place, as much of the vapour as possible should be brought into intimate contact with the condensed liquid, so that a state of equilibrium, as regards composition, may be brought about.

Brown's Formula.—Let us suppose, to facilitate the consideration of what occurs, that we are dealing with a mixture of two closely related compounds, to which Brown's

[fol. 1557] formula $\frac{m'_B}{m'_A} = c\frac{m_B}{m_A}$ is applicable, and that m' and

m refer to the weights of vapour and liquid respectively. Also let us suppose that, in the first place, equal weights of the two substances are taken, so that $m_A = m_B$.

Then the composition of the first small quantity of vapour formed will be given by the equation $\frac{m'_B}{m'_A} = c$ and the percentage of B in the vapour will be $\frac{c \times 100}{c+1}$.

If a distillation bulb with exceedingly short still-head be employed, this will practically be the percentage of B in the first portion of distillate.

Theoretically Perfect Still-head.—Suppose, now, that in the lower part of a long and theoretically perfect still-head condensation goes on, and that the condensed liquid remains in this part of the tube until its weight is, say, 100 times as great as that of the residual uncondensed vapour in the same part of the tube, the total weight of liquid and vapour being, say, 1/1000 of that of the mixture taken. We may then assume

1. That the composition of the liquid and vapour (taken together) in the still-head will be practically the same as that of the vapour first formed, and

2. That the composition of the condensed liquid will not differ sensibly from this, or $\frac{m_{1B}}{m_{1A}} = c$.

If the residual vapour is brought into thorough contact with the condensed liquid, its composition will practically be given by the equation $\frac{m'_{1B}}{m'_{1A}} = c \times c = c^2$, and the percentage of B in it will be $\frac{c^2 \times 100}{c^2+1}$.

[fol. 1558] weight of liquid and vapour in the still-head increases with the diameter of the tube, and it is therefore clearly more advantageous, in making a plain still-head, to use very narrow rather than very wide tubing. It will be noticed also that the narrowest tube gives a better result

than the tube of medium diameter nearly twice as long, though the weight of liquid and vapour is only 1.05 as compared with 3.55 grams

The diameter of the tubing cannot, however, be diminished beyond a certain amount, depending on the nature of the liquid distilled, especially on its boiling point, for if the tube is too narrow, the condensed liquid will unite into columns which will be driven bodily upwards. This blocking is much less liable to occur if a short piece of wider tube is sealed to the bottom of the narrow one. There must also be a wider piece at the top to admit the thermometer.

Condensation in the still-head may be diminished by covering it with cotton wool or any other non-conducting material, but while the amount of liquid in the tube is thus diminished, so also is the efficiency. The device is, however, occasionally useful, for if the liquid in the tube is just on the point of joining up into columns, the blocking may be prevented by slightly diminishing the amount of condensation.

Modifications of the Still-head.—It has been pointed out that the inefficiency of the plain vertical still-head is due to the want of thorough contact between the vapour and the condensed liquid, owing, firstly, to the central portion of the vapour passing rapidly up the tube and possibly never meeting with the liquid at all, and, secondly, to the condensed liquid flowing very rapidly back to the still. Consequently, any modification that brings about better admixture of the ascending vapour or that retards the down-flow of condensed liquid should increase its efficiency.

Sloping Still-head.—The simplest and most obvious alteration that can be made is to change the slope of the tube so as to retard the down-flow of liquid. This may be done by bending the tube near the top and bottom so that its ends remain vertical, while the middle part slopes very gently upwards.

It will be seen from Table 50 that, by altering a tube in the manner described, a notable improvement is effected, especially as regards the separation of the benzene, and [fol. 1559] it is remarkable that, although the down-flow of liquid is retarded, the quantity of liquid in the still-head is slightly diminished.

Spiral Still-head.—The efficiency is further improved by bending the sloping portion of the tube into the form of a spiral probably because a better admixture of the vapour is thus produced; by this device the amount of liquid in the still-head is still further reduced.[1]

"Rod and Disc" Still-head.—In the still-head shown in Fig. 42*a* the down-flow of part of the condensed liquid is greatly retarded by

[1] G. Berlemont, "New Tube for Fractional Distillations, modified by Lebel," *Bull. Soc. Chim.*, 1895, [III], 13, 674; *J. Soc. Chem. Ind.*, 1895, 14, 821.

5079

[fol. 1560] EXHIBIT No. 612

Dec. 16 1926.

Die Industrie

des

Steinkohlentheers

und

Ammoniaks

D EXHIBIT NO. 612

Von

Dr. Georg Lunge

Professor der technischen Chemie am eidgenössischen Polytechnikum in Zürich

Vierte Auflage

umgearbeitet und stark vermehrt

von

Dr. Hippolyt Köhler

technischem Chemiker für die Industrie des Steinkohlentheers

Erster Band

Steinkohlentheer

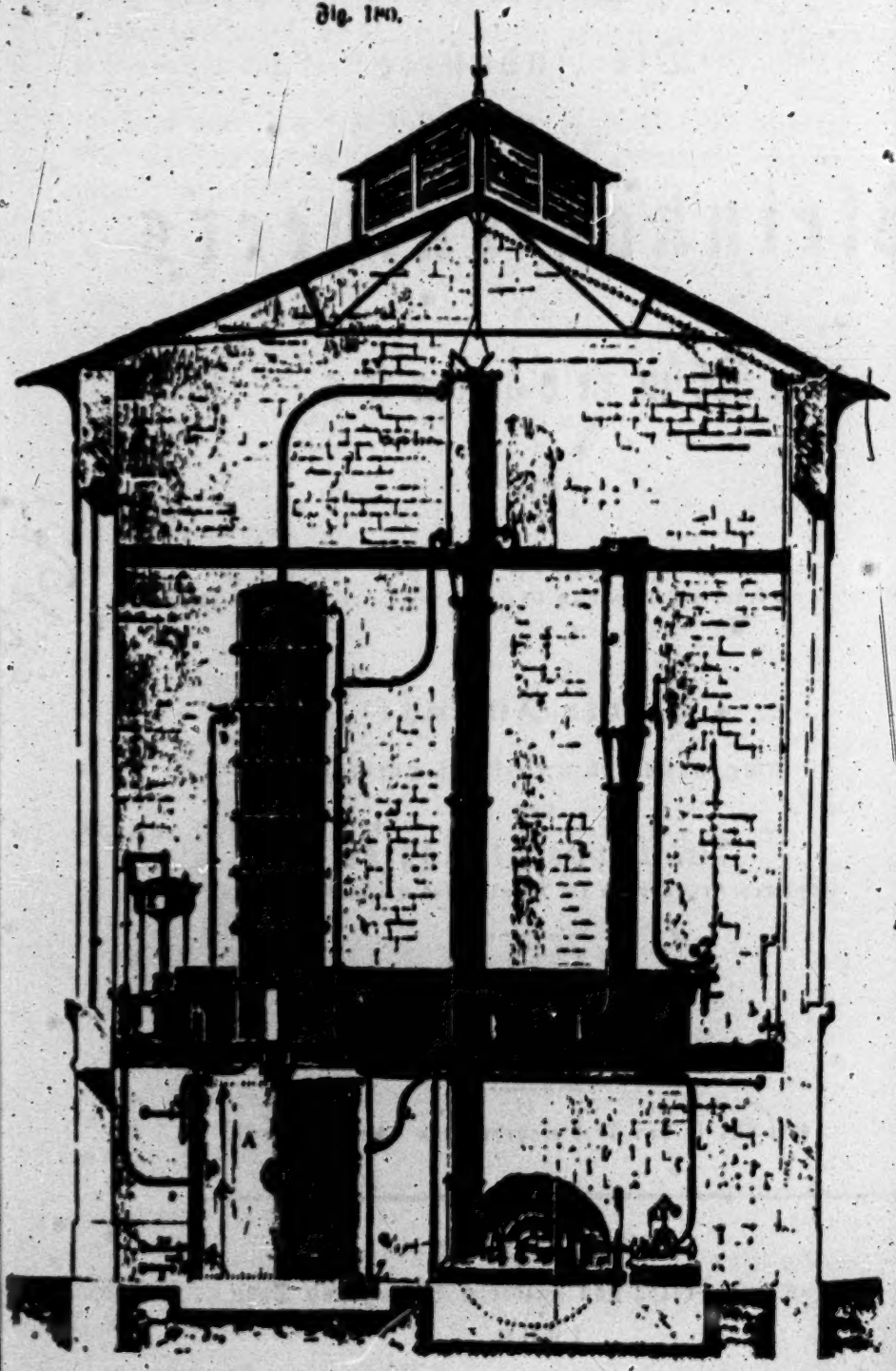
Mit 201 in den Text eingedruckten Abbildungen

Braunschweig

Druck und Verlag von Friedrich Vieweg und Sohn

1900

Fig. 180.



auch dieses aufhört zu fließen, so läßt man das Niveau des Wassers in *H* dadurch sinken, daß man hinter einander die Hähne g^1, g^2 g^3 und g^4 öffnet, so daß schließlich *H* ganz und gar mit Wasserdampf im Inneren der Röhren *dd* und mit den Dämpfen von Kohlenwasserstoffen in den Zwischenräumen um diese herum erfüllt ist. In diesem Stadium geht fast reines Xylol über.

Egrot's Apparat, welcher von Hohenhausen[1]) erwähnt wird, ist von dem Coupier'schen in keinem wesentlichen Theile verschieden.

Die Rectificationsapparate der Firma P. Savalle fils zu Paris genießen eines ausgezeichneten Rufes gerade auch für die Theerkohlenwasserstoffe und werden in Deutschland viel angewendet, auch in den Theerdestillationen selbst, wo man nicht auf die reinen Kohlenwasserstoffe, sondern auch auf 90- oder 50procentiges Benzol ꝛc. arbeitet. Der Apparat (Fig. 180) sei hier nach der von R. Meyer[2]) gegebenen Beschreibung und Abbildung wiedergegeben.

Bei Savalle's ursprünglichem Apparate wird die Condensation ganz und gar durch einen Luftstrom bewirkt, dessen Stärke durch ein Register regulirt wird; ferner enthält er die von derselben Firma schon früher bei der Spiritusrectification angewendeten Vorrichtungen zur Regulirung des Dampfdruckes und zur Controle der Destillationsgeschwindigkeit. Bei den für Benzolrectification bestimmten Apparaten hat man jedoch die Luftkühlung allenthalben durch Wasserkühlung ersetzen müssen, was uns auch von Häussermann (Priv.-Mitth.) bestätigt wird.

In Fig. 180 ist *A* die durch die Dampfschlange geheizte Blase, *B* die rechtwinkelige Colonne zur ersten Condensation, *C* der Luftcondensator zur zweiten Condensation der höher siedenden Kohlenwasserstoffe, welche nicht in das Destillat gelangen sollen, *D* der Luftkühler, in welchem sich das Destillat verdichtet und abkühlt. Die nöthige Luft wird durch den Ventilator *F* zugeführt, dem Condensator *C* durch *H*, dem Kühler *D* durch *I*. *J* ist das Register, durch welches der Luftstrom im Condensator mittelst einer Kette und eines gradnirten Hebels *K* regulirt wird. Die in *D* condensirte Flüssigkeit muß dann den Prober *G* passiren, in welchem der Gang der Destillation controlirt wird. *K* ist der Druckregulator, um während der ganzen Destillation einen constanten Druck im Apparate zu erhalten, *L* die den Ventilator treibende Dampfmaschine, *1* Dampfventil des Regulators, *2* Condensationswasserabfluß der Heizschlange, *3* Rückflußhahn der Colonne, *4* Reinigungshahn der Colonne, *5* Entleerungshahn des oberen Theiles der Colonne, *6* Thermometer, *7* Hahn für die Entleerung und Beschickung der Blase.

Die innere Einrichtung der Colonne zeigt Fig. 181 (a. f. S.). Die Dämpfe treten in dieselbe durch den cylindrischen Behälter *a*, welcher durch eine verticale Scheidewand der Höhe nach getheilt und mit einem Thermometer *b* versehen ist. Die Colonne ist durch horizontale, vielfach durchlöcherte Scheidewände in mehrere Kammern getheilt. In jede Scheidewand ist ein verticales Ueberlaufrohr eingesetzt, welches theilweise in eine entsprechende Vertiefung der

[1]) Journ. Soc. Chem. Ind. 1884, p. 70. — [2]) Volley-Birnbaum, Handb. d. chem. Technologie 5, 512 ff.

darunter liegenden Platte eingesenkt ist; diese Ueberlaufröhren sind abwechselnd an der einen und an der anderen Seite angeordnet. Die vom Condensator zurückfließenden, höher siedenden Producte passiren also allmälig sämmtliche Kammern der Colonne und gelangen schließlich in die Blase zurück. Die Durchbohrung der Platten ist so berechnet, daß der aufsteigende Dampfstrom die Flüssigkeit hindert, durch die Löcher hindurch zu fallen, und daher immer eine Flüssigkeitsschicht von 4 bis 5 cm Höhe (entsprechend den Mündungen der Ueberlaufröhren) auf den Scheidewänden zurückbleibt, welche die Dämpfe durch-

Fig. 181.

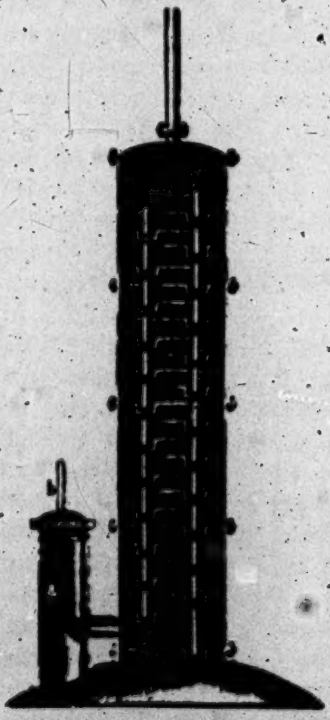
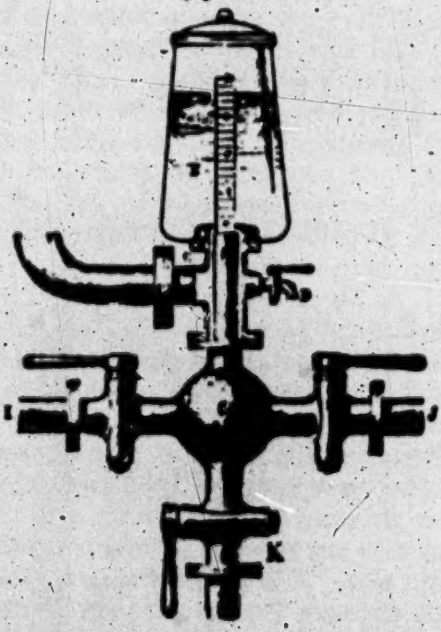


Fig. 182.



streichen müssen, nachdem sie die Löcher passirt haben. Dies begünstigt die Condensation der höher siedenden Producte bedeutend.

Fig. 182 stellt den Prober dar. Aus dem Kühler gelangt das Destillat zunächst in den ringförmigen Zwischenraum zwischen der Röhre C und der innerhalb derselben befindlichen engeren Röhre F. Diese ragt mit ihrem oberen, graduirten Theile in die Glasglocke E und hat bei F' eine kleine Oeffnung. Der Zwischenraum zwischen den Röhren C und F ist mit der Glocke E in Communication. Ist nun der Zufluß des Destillates ein solcher, daß letzteres bei dem im Apparate herrschenden Drucke durch F' abfließen kann, so wird die Flüssigkeit nicht über die Höhe dieser Oeffnung steigen. Ist aber die Zußlußgeschwindigkeit eine größere, so wird die Flüssigkeit aus dem ringförmigen Raume zwischen C und F in die Glocke E steigen. Hierdurch wird entsteht

ein hydraulischer Druck, welcher zur Folge hat, daß das Destillat durch die Oeffnung bei F schneller abfließt, als es ohne dies der Fall sein würde. So wird sich ein Gleichgewichtszustand herstellen, und man sieht ein, daß die Höhe der Flüssigkeitssäule in der Glocke E, welche man an der auf der Röhre F angebrachten Theilung ablesen kann, von der Zuflußgeschwindigkeit des

Fig. 183.

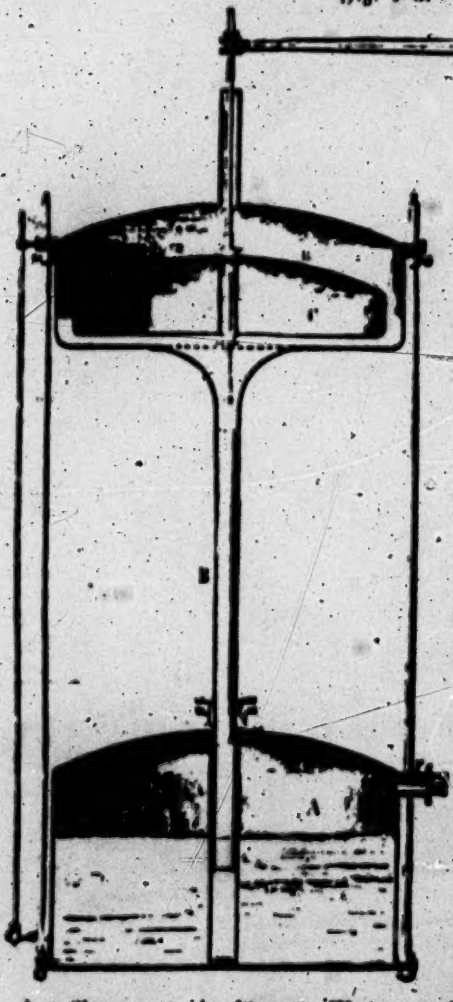
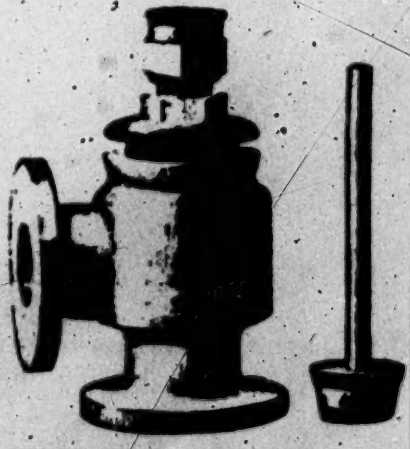


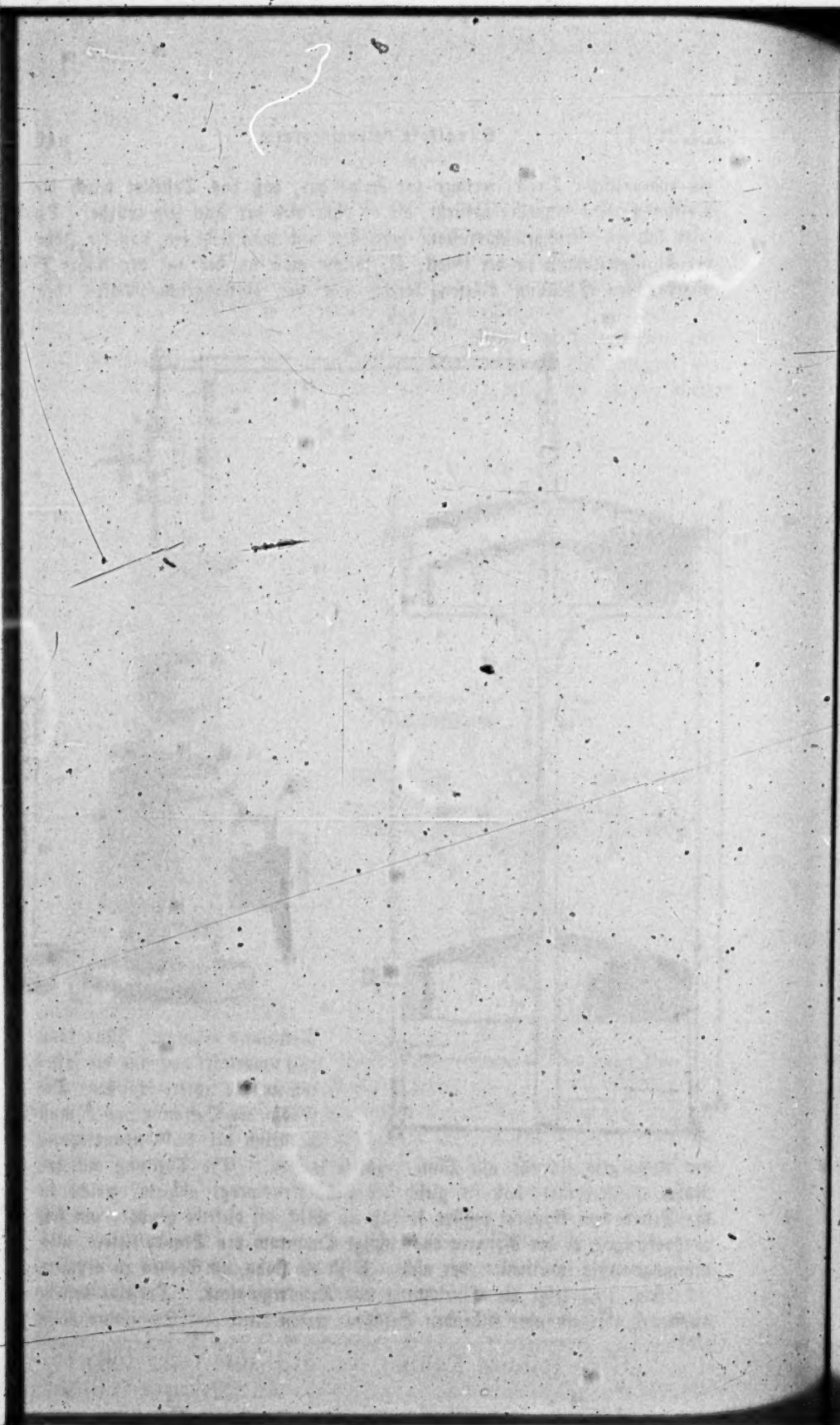
Fig. 184.



Destillates abhängt. Man kann also umgekehrt auch aus der ersteren auf die letztere schließen. Die Größe der Oeffnung von F muß natürlich bei der Ingangsetzung des Apparates ein für alle Male regulirt werden. Die Theilung auf der Röhre F ist derart, daß sie gleich die Flüssigkeitsmenge angiebt, welche in der Stunde den Apparat passirt, so daß ein Blick auf dieselbe genügt, um sich zu überzeugen, ob der Apparat das richtige Quantum pro Stunde liefert, also ordnungsmäßig functionirt oder nicht. D ist ein Hahn, um Proben zu nehmen.

Fig. 183 zeigt die Einrichtung des Druckregulators. Derselbe besteht aus zwei über einander stehenden Gefäßen, welche durch eine Steigröhre B in

(Here follows Exhibit No. 613, side folio 1565.)



[fol. 1565] EXHIBIT No. 613.

Dec. 16, 1926.

J. SCHNEIBLE.

DISTILLING COLUMN.

APPLICATION FILED AUG. 2, 1919.

1,366,956. Patented Feb. 1, 1921.

Fig. 1

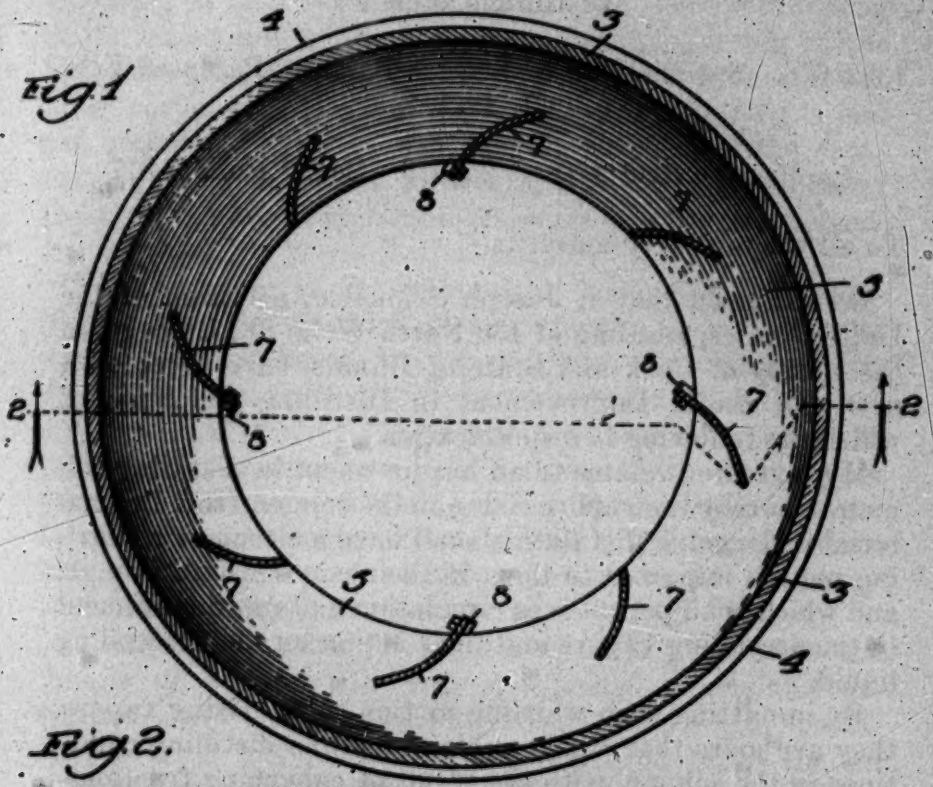
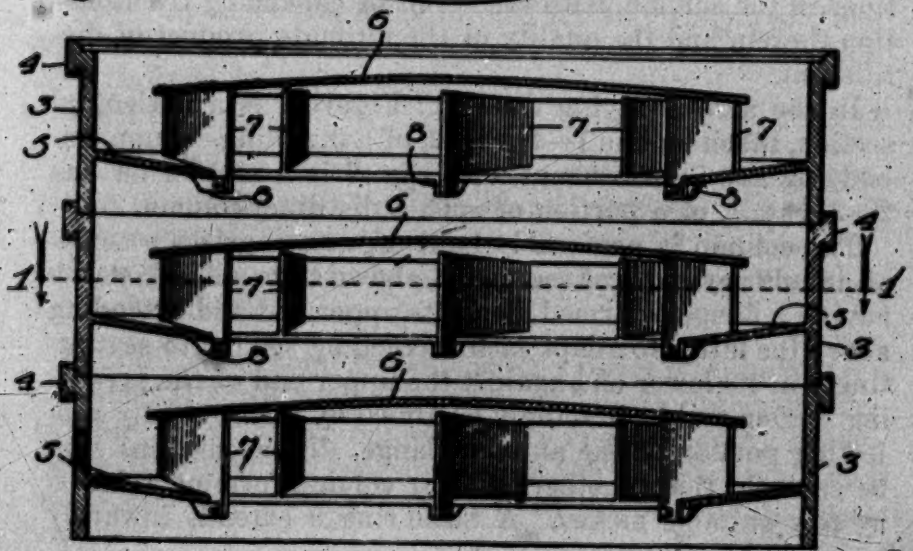


Fig. 2.



Inventor.
Joseph Schneible

[fol. 1566] United States Patent Office

Joseph Schneible, of Chicago, Illinois

Distilling-Column

1,366,956. Specification of Letters Patent. Patented Feb. 1, 1921

Application filed August 2, 1919. Serial No. 314,817

To all whom it may concern:

Be it known that I, Joseph Schneible, a citizen of the United States, residing at 130 North Wells St., Chicago, in the county of Cook and State of Illinois, have invented a new and useful Improvement in Distilling Columns, of which the following is a specification.

My invention relates to an improvement in distilling-columns whereby the vapors rising in the column from the material undergoing distillation shall have a circular or whirling motion imparted to them in their course therethrough, and which shall permit free circulation and rapid movement of the ascending vapors and their action on the descending liquid.

By imparting such whirling motion to the rising vapors, they are more thoroughly subjected to the distilling conditions in the column, with the result of enhancing fractionation therein and the quality of the ultimate product of distillation.

In the accompanying drawing, Figure 1 is a horizontal section, taken on line 1—1, Fig. 2, of a distilling-column embodying my improvement, and Fig. 2 is a section on line 2—2, Fig. 1, of a portion of such a distilling-column.

The column is preferably built of, or comprises a series of annular cylindrical sections 3, shown to be all alike, each having a flange 4 formed about its upper end and extending above the latter to adapt each succeeding section to seat fittingly at its lower end against the upper end of the preceding section and be bracingly encircled by the upwardly projecting portion of the annular flange. These sections may be securely tied together in their column-forming relation by any suitable means. A baffle-ring 5 extends inwardly

from the wall of each section 4 and inclines downwardly toward the center thereof. A concavo-convex deflector plate 6 has depending from it at uniform intervals, and formed integral therewith, a circular series of curved guide-vanes 7 bearing at their lower ends against and there conforming to the inclination of the baffle-ring, thus supporting on the latter the plate 6; and alternate vanes project at their lower inner corner-portions into the space within the ring 5, and are bolted to lugs 8 on the ring for reinforcing the vane-carrying deflector-plate structure, which forms an inner chamber open through circuitous courses to the outer chamber afforded by the respective chamber 3.

Vapors rising in the column-still encounter the lowermost baffle-ring 5, which directs them into the adjacent vane-chamber, wherein the vanes impart a whirling or circular motion to the rising vapors, and from which the plate 6 deflects the whirling vapors into the outer chamber of the particular column-section to be deflected by the next higher annular baffle-plate 5 and coursed in the same manner through the next-higher vane-chamber and column-section; and so on to the top of the still, where the vapors discharge as to a condenser (not shown).

I realize that considerable variation is possible in the details of construction thus specifically shown and described, and I do not intend by illustrating a single specific or preferred embodiment of my invention to be limited thereto; my invention being in the following claims to claim protection for all the novelty there may be in my invention as broadly as the state of the art will permit.

I claim:

1. A distilling column comprising a column containing a series of spaced annular baffle-plates, deflector plates, and stationary guide-vanes exposedly interposed between the deflector-plates and baffle plates and leaving unobstructed the baffle-plate openings.

2. A distilling column comprising a series of annular sections containing chambers, each comprising a lower annular baffle-plate, an upper deflector-plate and stationary guide-vanes exposedly interposed between the deflector-plate and baffle-plate and leaving unobstructed the baffle-plate opening.

3. A distilling column comprising a series of annular sections containing chambers, each chamber comprising a lower annular baffle-plate and an upper deflector-plate having a series of guide-vanes depending from it and extending to the baffle-plate.

4. A distilling column comprising a series of annular sections containing chambers, each chamber comprising a lower annular baffle-plate inclining downwardly toward the center of the section, an upper concavo-convex deflector-[fol. 1567] plate, and a series of guide-vanes between the deflector-plate and baffle-plate.

5. A distilling column comprising a series of interfitting annular sections containing chambers, each chamber comprising a lower annular baffle-plate inclining downwardly toward the center of the section and being provided with lugs at intervals, an upper concavo-convex deflector-plate, and a series of curved guide-vanes between the deflector-plate and baffle-plate, alternate vanes being fastened to said lugs.

Joseph Schneible.

exothermic. Figures 11, 12 and 13 show the nature of the heat changes occurring during the distillation of a few oil shales and a sample of lignite. About the only definite con-

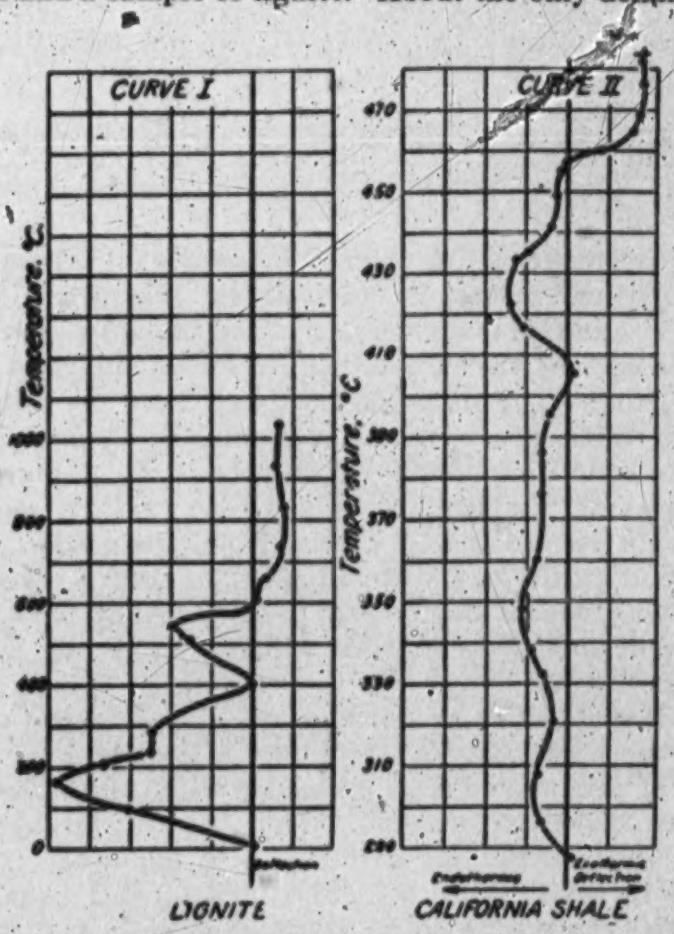


Fig. 13.—Heat changes on retorting lignite and lone, California shale.

clusion to be drawn from these curves is that commercial distillation procedure will have to be varied with the shale to be retorted and that no one method of retorting can be used equally well with all shales.

Cracking of the Oil during Retorting

The unusually high percentage of "unsaturated compounds" (compounds removed by treatment with concen-

trated 66° Bé—sulfuric acid) in shale oil has been explained by the low hydrogen content of the oil forming matter of the shales. The kerogen does not contain enough [fol. 1569] bitumen is unstable and a second decomposition changes it into the lighter oils of greater stability and higher "saturation." Experimental work has shown that the stability, specific gravity, viscosity, volatility and "saturation" of the oil produced increase as the decomposition of the intermediate product increases. Both the primary and secondary decompositions are accompanied by a series of thermal reactions. The formation of oil from oil shale thus takes place as follows: kerogen—intermediate bitumen —shale oil.

The percentage of "saturates" of a shale oil is increased by distillation to coke at atmospheric pressure. Corresponding with this is an increase in the amount of low boiling fractions in the distillates. Evidence indicates (see Fig. 18) that crude shale oils produced from the retort at ordinary rates, are mixtures of secondary decomposition products and of undecomposed or only partly decomposed "intermediate bitumen" which has been carried from the retort with the gas and oil vapors during distillation. The increase in quality of a shale oil resulting from a redistillation of the crude oil may largely be explained by the decomposition of this undecomposed bitumen in the oil during the redistillation.

The decomposition or cracking of well petroleum under the influence of heat and pressure is accompanied by a change of products of high molecular weight into products of lower molecular weights. This cracking always decreases the amount of "saturates" in the lower boiling product formed. When a highly "unsaturated" shale oil is cracked, the results obtained are apparently just the reverse of those obtained with petroleum.

The cracking of well petroleum and shale oil petroleum are not entirely parallel processes, however. Well petroleum is ordinarily a mixture of a great number of hydrocarbons of different molecular weights and degrees of complexity. When these are heated, the least stable hydrocarbons—those of high molecular weight and great molecular complexity—break down into simpler forms, yielding both saturated and unsaturated hydrocarbons, the net result

being that the cracked distillate is more or less unsaturated, i. e., really contains unsaturated hydrocarbons, whereas the original oil was practically completely saturated, i. e., contained no unsaturated hydrocarbons. A shale petroleum, on the other hand, contains saturated and unsaturated hydrocarbons, and in addition relatively large amounts of oxygen, [fol. 1570] nitrogen and sulfur compounds, which are not hydrocarbons but are measured as "unsaturates" by the sulfuric acid test. Some such shale oils contain over 10 per cent of basic nitrogen compounds which may be removed with quite dilute acid. When shale oil is cracked, undoubtedly some of the complex and heavy saturated hydrocarbons decompose to produce both saturated and unsaturated hydrocarbons, and some of the complex unsaturated hydrocarbons break down to form both saturated and unsaturated hydrocarbons of simpler structure. Finally a part of the relatively unstable oxygen, sulfur and nitrogen compounds in the oil, which have been measured as "unsaturates," break down, yielding both saturated and unsaturated hydrocarbons, while the oxygen, nitrogen and sulfur may be eliminated to a greater or less extent. The net result is an indicated gain in "saturates" (insoluble in concentrated sulfuric acid). The gain is actual, but it is not alone because unsaturated hydrocarbons have been saturated or broken down to form simpler saturates during the cracking. A part of the gain is that compounds measured as "unsaturates" by test with a concentrated acid, are not all unsaturated hydrocarbons, but compounds which decompose on heating to yield "saturated" hydrocarbons. Distillation of shale under pressure (300 pounds per square inch) has been shown to increase cracking of the oil. If the process is carried out slowly the resulting distillate is as clear as water and of much lighter gravity than distillate from oil shale made at atmospheric pressure. Whether such a slow distillation at such a pressure could be carried out commercially is extremely doubtful.

The Action of Solvents on Oil Shales

The understanding of the composition of oil shale kerogen would be greatly advanced if any considerable part of it

were found to be preferentially soluble in any given solvent. Little work of this nature has thus far been reported, however, and solubility studies apparently have shed little light on the composition of kerogens. Table III[914] gives the solubilities of a few typical oil shales in some of the common organic solvents, and shows that little of the organic matter of the shales can be obtained by extraction with these solvents. Different shales, however, show different solubilities, and this is another example of the fact that kerogens of different shales are not similar.

[fol. 1571] Experimental work thus far reported on the action of solvents and reagents on oil shales indicates that it will never be commercially feasible to produce oil from shales by extraction with organic solvents or by the action of chemical reagents of the ordinary type. This is to be expected as oil does not exist as such in true oil shales. Apparently the only practical method for the production of oil from oil shales is by the action of heat.

Action of Chlorine on Oil Shales

Hart (see Chem. Zeit., 30, 1204 of 1906) has shown that chlorine, bromine and iodine are absorbed by different [fol. 1572] coals, thus indicating the

presence in the coals of different proportions of compounds containing unsaturated groupings. When lignite is treated with chlorine or bromine without external heating, the temperature increases to 90°-100° C. If the product of the resulting reactions is extracted with carbon disulfide, a halogen-containing resinous substance is obtained. Cross and Bevan have shown that coal is attacked by chlorine with the production of a chlorinated derivative similar to that previously obtained by them from lignified tissue. A shale oil obtained by distillation often contains 50 to 75 per cent of "unsaturates," so chlorination experiments[1017] were performed to determine if the unsaturated groupings are present in the organic matter of the shale, or if they are produced as decomposition products by the heat treatment; and to determine if it was possible to obtain little complicated chlorine products and to identify these products.

Shale from De Beque, Colo., was suspended in carbon tetrachloride and chlorine gas passed through the solution

for 36 hours. The solution was filtered through an alundum crucible, dried and weighed. The increase in weight resulting from this chlorine treatment was 0.59 per cent. The same sample of shale was then extracted with absolute alcohol in a Soxhlet extraction apparatus until the returning solvent was colorless. This solvent extracted 6.23 per cent from the chlorinated shale, calculated on the weight of the original shale. The same solvent extracts but 1.43 per cent from this shale before chlorination.

Shale from Ione, California, is soluble but 6.9 per cent in absolute alcohol. If treated with chlorine the percentage soluble was increased to 41.3 per cent. Efforts to identify this soluble material were unsuccessful. It is, however, apparent that the vigorous action of the chlorine gas on the powdered shale with the formation of an alcohol soluble organic material is ample evidence for the presence of unsaturated groupings in the organic matter of the shale.

Sulfuryl chloride reacts with higher olefins to yield dichlorides[1017]. Powdered shales treated with sulfuryl chloride at the boiling point of the latter (69° C.) were reacted upon and the organic matter chlorinated. Shale so treated was increasingly soluble in absolute alcohol. Efforts to identify these chlorine derivatives were unsuccessful but indicated that they were of the same general character as those formed by treating the shale with chlorine gas, i. e., [fol. 1573] chlorine derivatives of unsaturated compounds present in the organic matter of the oil shale.

Microscopic Study of a Few Typical Oil Shales

Under the microscope an American oil shale shows many laminations of dark brown to reddish colored material, separated by bands of almost colorless inorganic material. The bands of darker material usually are

[fol. 1574] Table III

Comparison of Shale Oils Made in Testing Retort with Scottish Shale Oil Produced Commercially, and Average Quality Petroleums from the Pennsylvania and Mid-Continent Districts

Source of oil	1. Scottish shale	2 Scottish shale	3 Shale from	4 Pennsyl-	5 Typical
How produced	Scottish commercial retort	Testing retort	Soldiers Summit, Utah Testing retort	vania crude Oil well	Mid-Continent crude Oil well
Retorting Time	6-8 Hrs.	2 Hrs.	5 Hrs.		
Yield of oil	....	18.1	40.2	....	....
Specific gravity of oil	0.867	0.864	0.882	0.812	0.835
Setting point of oil, Deg. C.	28	32	33	....	....
Distillation, first drop, Deg. C.†	49	44	40	26	30
Per cent distilled to 200 Deg. C.	12.22	16.63	18.81	31.93	28.0
Unsaturation, 200 Deg. C. fraction, per cent	28.0	34.1	40.2	3.6	4.0
Per cent distilled, 200-275 Deg. C.	23.22	20.47	20.10	20.83	15.0
Unsaturation, 200-275 Deg. C. fraction, per cent	34.0	34.1	40.2	3.6	4.0
Vacuum fraction to 200 Deg. C.:					
Per cent	9.32	2.10	2.64	3.33	4.0
Specific gravity	0.872	0.868	**	0.826	0.850
Viscosity	38	38	**	39	41
Setting point, Deg. C.	*	*	*	*	*
Vacuum fraction 200-225 Deg. C.:					
Per cent	5.27	4.38	7.80	7.75	6.0
Specific gravity	0.881	0.872	0.880	0.832	0.855
Viscosity	40	41	42	40	47
Setting point, Deg. C.	*	*	*	*	*
Vacuum fraction 225-250 Deg. C.:					
Per cent	7.16	5.88	9.20	6.02	7.0
Specific gravity	0.892	0.874	0.889	0.841	0.865
Viscosity	46	43	48	45	60
Setting point, Deg. C.	24.5	21.5	18	15.5	15
Vacuum fraction 250-275 Deg. C.:					
Per cent	6.13	7.30	14.90	5.37	4.0
Specific gravity	0.902	0.894	0.906	0.848	0.875
Viscosity	52	50	58	51	80
Setting point	29	29	31.5	22.5	20
Vacuum fraction 275-300 Deg. C.:					
Per cent	6.07	9.45	8.88	5.16	6.0
Specific gravity	0.911	0.898	0.928	0.859	0.890
Viscosity	60	60	72	67	130
Setting point, Deg. C.	34	37	40	30	30

*Not determined.
**Combined with next higher cut.
†Fixed-gas gasoline not included in crude used for these distillations.

[fol. 1575]

Chapter 6

The Refining of Shale Oils

By E. E. Lyder

Shale oil is the product obtained by the destructive distillation of oil shale kerogen. The composition and character of shale oil are dependent on the manner in which it is produced from the shale as well as on the characteristics of the shale and pyrobitumen from which the oil is made. Although the shales of this country and therefore the shale oils made from them are different from those of Scotland, certain fundamental practices used there will undoubtedly be applicable here. By adopting the desirable points of Scottish shale oil and American petroleum refining practice and solving the special problems presented by each shale (being careful to choose the desirable shales) the refining of shale oil offers no unsurmountable difficulties.

The first product of the decomposition of the pyrobitumen in oil shale is a semi-solid asphalt-like material (a bitumen) which breaks down to produce shale oil. The exact nature of this bitumen is not definitely known but it has been shown that it is composed mostly of substances soluble in concentrated sulfuric acid.[1017] When this semi-solid asphalt-like material is converted into crude oil by the process of distillation, the product formed is only partly soluble in sulfuric acid. The oil coming from a shale retort may contain as much as 50 to 80 per cent of "unsaturated" compounds, depending again on the method of distillation. Those processes which approach destructive distillation will produce an oil containing the maximum amount of "saturated" compounds, while those which approach the process of simply distilling over the bitumen give the more "unsaturated" oils. (See Fig. 18.)

When shale oils are refined, the crude oil comes to the refinery as a more or less unstable material and the refining process must be such that it will not only separate this crude oil into its various products and remove the objectionable impurities, as in petroleum refining, but it must also convert as much as possible of the crude oil into stable products. This is accomplished to a large degree by successive distillations. The first distillation of the crude will yield a larger portion of "saturated" compounds and if it be distilled again, more "saturated" products will be pro-

duced, and so on until the oil contains the minimum amount of compounds soluble in strong sulfuric acid. The following example illustrates this point.

[fol. 1576] The "unsaturation" (amount soluble in an excess of 1.84 sp. gr. sulfuric acid) of a crude oil from a commercial shale oil plant was 75 per cent. This oil was distilled to dryness in a one-pint cast iron mercury retort and the "unsaturation" of the distillate had now been reduced to 57 per cent. This distillate was again distilled and the "unsaturation" of the resulting product was 50 per cent. A fourth distillation reduced the "unsaturation" to 49 per cent, or practically the same as the third distillation. This shows one way in which shale oil changes character as a result of distillation. A further example of this change is the following data which were taken from the records of a commercial plant (Catlin Shale Products Co., Elko, Nev.).

	Soluble in concentrated acid, per cent
Crude Oil (Directly from the retort)	77
Once-Run Oil (The crude distilled to dryness without steam)	65
Re-Run Oil (The once-run distilled to dryness without steam)	53
Slack Wax (The crude wax containing oil)	21
Cold Pressed Distillate (Oil with all wax removed)	21
Gasoline Fraction (Topped from the cold pressed distillate)	30
Gas Oil (Topped from cold pressed distillate after gasoline fraction had been removed)	46
Lubricating Stock (Untreated)	40

Throughout the whole operation of retorting and refining, the production of crude and refined products from shale and shale oil can be considered as nothing more or less than the production and cracking of a heavy bitumen to produce lighter oils. Although the process takes place at atmospheric pressure it is none the less a cracking process, and thus a considerable refining loss must be expected. The high percentage of unsaturated compounds in the various cuts results in high treating losses as well as excessive carbon deposits when the oils are distilled to dryness. In Scottish shale oil refining practice, the loss, including coke, and gas amounts to about 24 per cent of the crude oil.

So much has been written about the refining of shale oils in Scotland that it is unnecessary to go into detail here, but a brief summary will be given. The refining process carried out by the Scottish Oils, Limited, is characterized by the running of small batches of oil in relatively small stills and by the large number of cuts made. Steam is used in all distillations except at the end of the coking distillations.

The oil is first settled free from shale dust and ammonia water and

[fol. 1577] will be called upon to furnish only a part of the supply. Gasoline made by cracking the heavier fractions of petroleum is now used extensively to supplement the inadequate supply of straight-run gasoline. Cracked gasoline is usually not put on the market as a straight cracked product but is blended with casinghead or other low boiling point gasolines. Shale gasoline, whether produced directly from shale oil or by the cracking of the heavier fractions in pressure stills (Burton, Dubbs or other types) is a cracked product and must be handled in all respects as such.

Gasoline of proper volatility and free from gum forming compounds, excessive carbonizing properties and unpleasant odor can be produced from petroleum by treating with acid and caustic and steam distillation. With shale gasoline the same scheme will be followed except that more distillations and more treatments will be necessary. Since more unsaturated compounds are present in shale gasoline fractions, the loss on treatment with strong sulfuric acid is considerably greater than when gasolines are refined from petroleum.

Certain unsaturated compounds, such as some of the olefins, are not objectionable while others, the diolefins, are detrimental in the finished products. The refining process should be devised to remove only the detrimental constituents from the gasoline. An excess of strong sulfuric acid readily attacks certain members of the olefin series, removing them from the gasoline. Thus the acid is used up without completely destroying the coloring materials and strong smelling compounds present. For this reason the use of an excess of 66° Bé. acid results in high refining losses without thoroughly clarifying and deodorizing the gasoline. The gasoline may be effectively treated with

various clays and color-removing compounds. Contact filtration with certain of these acid-activated clays or color-removing compounds together with treatment with relatively small amounts of sulfuric bids fair to be the ultimate method for refining a number of shale oil products. Especially effective are those activated materials which remove the various organic sulfur compounds which are present in shale gasoline to a greater or less extent, depending on the character of the shale from which the oil is made. Among the materials which may be used are the specially activated clays, absorbent carbons, activated fuller's earth, and silica gel. The hypochlorite wash used by some petroleum refineries for sulfur removal offers possibilities in connection with shale oil refining.

[fol. 1578] The use of catalysts in the production and refining of gasoline has not been marked with success. In fact, the aluminium chloride process is the only well known catalytic process used in the petroleum cracking industry. When it is properly applied, this process, at atmospheric pressure, converts heavy hydrocarbons into lighter ones and yields the much desired saturated products. This, added to the fact that aluminium

[fol. 1579] Present Status of the Development of American Oil Shale Lands

The comparatively rapid exhaustion of our natural petroleum supplies, as well as the great magnitude of the oil shale deposits in Colorado, Utah and Nevada, has created a tremendous interest in the development of oil shale lands and processes. Over two hundred and fifty companies have been listed at Mellon Institute of Industrial Research during the last few years and since 1914 over one hundred and fifty patents have been issued, that describe alleged novel processes of getting crude oil from shale. Of the two hundred and fifty companies, some twenty have erected experimental plants, mostly quite small, and there is now no really commercial production of shale oil in this country, except possibly by the Catlin Shale Products Co. Inquiry has shown that a number of the companies are "wild-cat," stock-promotion ventures of the worst character. Other companies with honest intentions do not in many cases have good technical advice. The American people are warned that the difficulties of obtaining crude oil from

shale at a profit are very great, and that it may be years before a successful shale oil plant assumes commercial importance in this country.

Speaking generally, the crude oil produced by the destructive distillation of oil shale resembles petroleum somewhat, but it is by no means identical with petroleum. For one thing, it is usually much more difficult to refine by the customary processes than petroleum. The only place in the world where there has ever been a truly successful shale oil industry of any size is in Scotland, and study of the Scottish experience demonstrates that technical men—chemical and engineering specialists—must have time to work out the many problems connected with an American shale oil industry. That research is not yet done, and until it is accomplished the immense American tonnage of oil shale must be regarded as an oil reserve for the future and not as a present supply. A number of technical observations have been announced by American experimenters as discoveries of importance which are not new, because the men who have made them do not possess the requisite fundamental knowledge. This situation has had a rôle in making something of a mystery out of certain operations that are well known to students of Scottish shale oil technology.

[fol. 1580] No sound contention can be made that any type of Scottish dual-purpose retort[459] should constitute the actual basis for the development of an American shale oil industry, for this retort is not the design that is required today to handle most economically all grades of oil shale; but it is essential that more careful consideration be given to Scottish experience in retorting practice as well as in general oil shale technology. This successful experience, and the misfortunes of those who attempted

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Endorsed on cover: File No. 35,300. N. Illinois D. C. U. S. Term No. 378. Standard Oil Company (Indiana), Standard Oil Company (New Jersey), Standard Development Company, et al., appellants, vs. The United States of America. Filed August 23, 1930. File No. 35,300.